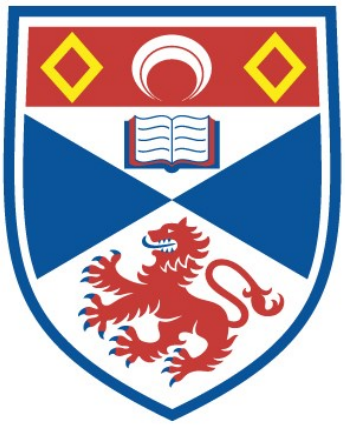
SOME ASPECTS OF ORGANO-PHOSPHORUS, -ARSENIC, AND -ANTIMONY HALIDES

Mohammad Farhat Ali

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1968

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A Thesis

presented for the degree of

Doctor of Philosophy

in the Faculty of Science of the

University of St. Andrews

by

Mohammad Farhat Ali, M.Sc., A.R.I.C.

May, 1968.

United College of St. Salvator
and St. Leonard, St. Andrews.

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I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a higher degree.

The thesis describes results of research carried out in the Chemistry Department of St. Andrews University during the year beginning 1st October, 1965, under the supervision of Dr. G.S. Harris.

I hereby certify that Mohammad Farhat Ali has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research.

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C O N T E N T S

FIGURES

TABLES

T A B L E S cont.

GENERAL INTRODUCTION

Amongst the first organometallic compounds to be prepared and studied were the trialkyl and triaryl derivatives of the elements phosphorus, arsenic, antimony and bismuth[1]; and early on in the study of these compounds it was recognised that many of them reacted with halogens to produce adducts of the type R_3MHal_2 [2] (R = alkyl or aryl group; M = Group VB element).

These tertiary organoelement dihalides, which are well known for phosphorus, arsenic, antimony and bismuth can be considered as members of the more general series R_nMHal_{5-n} (n = 0 to 5), the extremes of which are the pentahalides, $MHal_5$, and the fully substituted organic derivatives, R_5M. The nature of these compounds has been discussed from time to time, [3-7] and they are known to exhibit a considerable variety of structures, depending on the physical state and nature of substituent groups. The pattern of structures and properties among these related group VB compounds is briefly outlined in the following paragraphs.

Many of the pentahalides of this group of elements are found to be capable of existing in two different structural forms, one of which is molecular and the other ionic. For example, structural investigations have demonstrated the presence of trigonal bipyramidal molecules in the molecular forms (e.g. in PF_5(g), (l); PCl_5(g); AsF_5(g), (l); SbF_5(g); $SbCl_5$(g), (s)), whilst the ionic forms have a halogenophosphonium salt type of structure (e.g. PCl_5(s) is $PCl_4^+ PCl_6^-$; PBr_5(s) is $PBr_4^+ Br^-$). Although certain of the pentahalides appear to exhibit only a molecular form (e.g. PF_5) others possess duality of behaviour being ionic under certain conditions and molecular under others (e.g. PCl_5 is ionic in the solid

state, and molecular in liquid and vapour phase). This duality in behaviour extends to the behaviour of the compounds in non-aqueous solvents where it is found that in non-polar solvents the molecular form is present [8] whereas in polar solvents the ionic form predominates.[9,10]

Known compounds of the fully substituted pentahalides (R_5M) are rare, being restricted to the pentaphenyls,[11] related derivatives in which four of the co-ordination sites of M are occupied by two biphenylene groups,[12] and some penta-alkenyls.[13] A recent X-ray analysis of pentaphenylphosphorus has shown that like the molecular forms of the pentahalides the structure is based on trigonal bipyramid units in which the apical P-C bond lengths (1.987Å) are slightly longer than the equatorial bond lengths (1.850Å) [14]. Pentaphenylarsenic is isomorphous [15] with the phosphorus compound., but pentaphenylantimony has anomalously tetragonal pyramidal geometry[16]; this is of considerable interest as it seems to be the only well established example of this stereochemistry in a five-coordinate compound of a group V element.

The structure of organosubstituted pentahalides of the type $RMHal_4$ and R_2MHal_3 is not so clearly established and it is conceivable that they might exist in both trigonal bipyramidal and in ionized forms. From their low melting points and ease of solubility in organic solvents, Rochow et. al. [6b] describe such compounds to be covalent in nature. On the other hand Van Wazer, [7b] by analogy with the pentahalides of phosphorus, suggests the ionic structure $[RPHal_3]^+ Hal^-$, for halophosphine halides of

the type $RPHal_4$. Kosolapoff [3b] agrees with Van Wazer's views that one of the halogen atoms is in the ionic state. This view is further supported by the behaviour of certain $RPHal_4$ derivatives (e.g. $PhPBr_4$, $PhPBr_2Cl_2$) which add another mole of halogen to form compounds of the type $RPHal_6$, [17] analogous to those formed between the ionic quaternary salts and the halogens. Similarly, R_2PHal_3 ($R = C_2H_5$, C_3H_7) reacts with halogens to form R_2PHal_5, which have been shown to give conducting solutions in polar solvents indicating a dihalophosphonium salt type of structure ($R_2PHal_2^+ Hal_3^-$) for these compounds. [18]

There now appears to be fairly firm evidence for both ionic and covalent forms in the $RMHal_4$ and R_2MHal_3 group of compounds. For example, chloro-organo phosphonium cations of the type postulated for the ionic forms of $RPHal_4$ and $RPHal_3$ have been demonstrated recently, by ^{31}P - NMR studies, to be present in the compounds $[Ph_nPCl_{4-n}]ClO_4$ and $[Ph_nPCl_{4-n}]SbCl_6$. [19] Also, recent ^{19}F - NMR investigations of a considerable number of fluoro-phosphoranes (e.g. RPF_4; $R = CH_3$, C_2H_5, $\underline{n}$-C_4H_9, Ph) and a few of the analogous arsenic and antimony compounds suggest trigonal bipyramidal structure for these compounds. [20,21] The structures of gaseous CH_3PF_4 and $(CH_3)_2PF_3$ have been determined by electron diffraction, [22] and that of crystalline Ph_2SbCl_3 by x-ray diffraction, [23] with the same results.

The structure of the derivatives R_3MHal_2 has been discussed from time to time by various authors. In particular, Harris and co-workers[24-26] have made an extensive study of halogen adducts of the triaryl derivatives of group VB elements. They have shown from their conductometric measurements in methyl cyanide solutions that the phosphorus dihalides are strong electrolytes and the antimony and bismuth dihalides non electrolytes, and have suggested that the solids are respectively ionic and covalent. Triarylarsine dihalides on the other hand are weak electrolytes and therefore probably covalent in the solid state. The ions present in these conducting solutions of Ph_3AsHal_2 and Ph_3PHal_2 have been the subject of some study. From the measurement of ion transport numbers of the methyl cyanide solutions Harris et al.[25] have demonstrated that Ph_3AsCl_2 and PH_3AsBr_2 ionise as follows.

$$2\ Ph_3AsCl_2 \rightleftharpoons [Ph_3AsCl]^+ + [Ph_3AsCl_3]^-$$

$$Ph_3AsBr_2 \rightleftharpoons [Ph_3AsBr]^+ + Br^-$$

That is, different modes of ionisation are adopted by the chloride and bromide; this behaviour is reminiscent of that of phosphorus pentachloride ($\longrightarrow PCl_4^+ + PCl_6^-$) and phosphorus pentabromide ($\longrightarrow PBr_4^+ + Br^-$) in the same solvent.[9,10]

Triphenylphosphorus dihalides have recently been shown by ^{31}P - NMR study[27], and from their reactions with the strong chloride ion donor, tetraethylammonium chloride[28], to ionise completely in methyl cyanide in the sense;

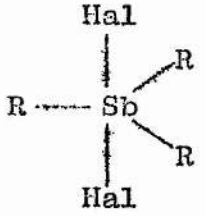
$$Ph_3PHal_2 \rightleftharpoons [Ph_3PHal]^+ + Hal^-$$

and there is no evidence for the alternative:

$$Ph_3PHal_2 \rightleftharpoons [Ph_3PHal]^+ + [Ph_3PHal_3]^-.$$

The existence of the halotriorganophosphonium cation, $[R_3PHal]^+$, in the tertiary phosphorus dihalides, R_3PHal_2 (R = Et, Pr, Bu, iso-amyl, cyclohexyl, or Ph) has also been inferred from their solubility behaviour, their high decomposition temperatures, and the electrical conductivities of their nitrobenzene solutions.[29] Some addition compounds of tertiary phosphorus dihalides with metal halides, $MHal_n$ [e.g. M = Sb(V), Sb(III), Hg(II)], have been prepared and they too would appear to be derived from a phosphonium-type structure, $[R_3PHal]^+[MHal_{n+1}]^-$; they have high melting points, are insoluble in non-polar solvents, and their nitrobenzene solutions are good electrolytic conductors.

The trimethylphosphine dihalides Me_3PHal_2 (Hal = Cl, Br, I) have been the subject of spectroscopic studies from which it has been shown that in the solid state ionic structures of the type $[Me_3PHal]^+Hal^-$ are adopted.[30] In contrast with this trimethyl-, triethyl-, and triphenyl antimony dihalides would seem to have D_{3h} symmetry indicating the trigonal bipyramidal structure [1] [31,32].



[1]

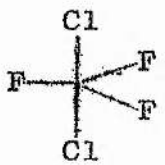
This latter geometry has in fact been established by x-ray crystal structure analysis for $(CH_3)_3SbHal_2$(Hal = Cl, Br, I)[33], $(ClCH{:}CH)_3SbCl_2$[34], Ph_3SbCl_2[35] and Ph_3BiCl_2[36].

Triphenylarsenic dichloride may well have a similar structure as its dipole moment in benzene solution is zero.[37]

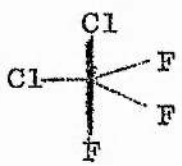
A large number of quaternary substituted compounds (R_4MHal) are known for phosphorus, arsenic and antimony. They are high melting crystalline solids, soluble in polar solvents in which they give highly conducting solutions, suggesting therefore that they are ionic, both in the solid state and in solution. An investigation of the crystal structure of Ph_4PI has shown that the structure is built from tetrahedral Ph_4P^+ and I^- ions.[38] There is no evidence of an R_4MHal type compound exhibiting a covalent structure.

Geometrical Isomerism in the Molecular Pentahalides of Group VB Elements:-

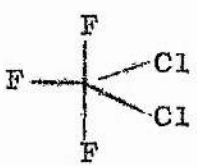
In the case of molecular mixed pentahalides, MX_nY_{5-n}, and organo-substituted halides, MR_nHal_{5-n}, there arises the possibility of stereo-isomerism because of the non-equivalence of axial and equatorial positions in a trigonal bipyramid. This is something not appreciated till relatively recently and not much attention was given to it. For example, three different types of structures are possible for the molecule PF_3Cl_2.



[a]



[b]



[c]

Early electron diffraction studies [39] of PF_3Cl_2 indicated a D_{3h} trigonal bipyramid, structure [a], in which the F-atoms occupy the equatorial positions. Some NMR studies [40] led to the same conclusions. However, more recent NMR work [20,21] indicates the presence of fluorine atoms with two kinds of environment and the structure [c] was proposed. Recent low-temperature Raman and vapour phase IR investigations [41], also indicate PF_3Cl_2 molecules with C_{2v} symmetry.

A number of workers have now made extensive spectroscopic studies of substituted phosphorus (V) fluorides, some of the results are summarised in Table I, overleaf.

From this, the rule emerges that the more electronegative ligands would always assume apical positions in trigonal bipyramid. This rule holds for all trigonal bipyramidal structures that have been investigated and reported in the literature, and to date there are no exceptions.

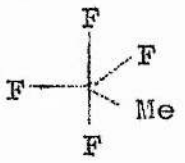
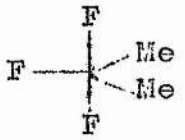
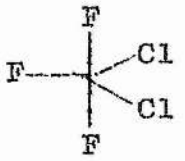
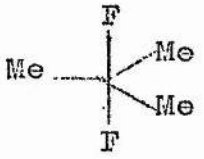
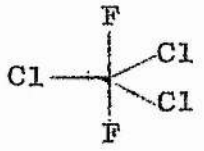
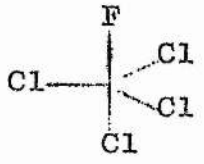
These mixed pentahalides also show ionic-covalent isomerism of the type shown by simple halides PCl_5 and PBr_5. For example, PCl_2F_3 is a gas at room temperature and is formed in the vapour phase reaction [44]:

$$PF_3 + Cl_2 \longrightarrow PCl_2F_3.$$

The isomeric salt like compound has the structure $[PCl_4]^+[PF_6]^-$ and can be prepared quantitatively by the action of arsenic trifluoride on phosphorus pentachloride dissolved in arsenic trichloride [45].

$$[PCl_4]^+[PCl_6]^- + 2AsF_3 \longrightarrow [PCl_4]^+[PF_6]^- + 2AsCl_3$$

Table 1. Stereochemistry of Fluorophosphoranes

	Compound	State*	Structure	Method✓	Reference
1.	PF_4Me	g,l		E.D., IR, NMR	22,21,42,55
2.	PF_3Me_2	g,l		E.D., R, IR, NMR	22,21,43,55
3.	PF_3Cl_2	g,l		R, IR, NMR	20,21,41,54
4.	PF_2Me_3	l		R, IR, NMR	21,43,55
5.	PF_2Cl_3	g,l		R, IR, NMR	20,41,54
6.	$PFCl_4$	g,l		R, IR, NMR	41, 54

*g, gas: l, liquid.

✓ E.D. Electron diffraction; R, Raman; IR, Infrared; NMR, ^{19}F - NMR

Unlike the gaseous molecular compound PCl_2F_3 (boiling point 8°) this isomer is a white solid which sublimes at 135°, and is sparingly soluble in arsenic trichloride. The conductivity of molecular PCl_2F_3 in methyl cyanide is small [46], whereas that of $[PCl_4]^+[PF_6]^-$ is relatively high [45]. When sublimed the compound $[PCl_4]^+[PF_6]^-$ changes to the gaseous covalent compounds PF_5 and PCl_4F [47]. PCl_4F is not stable over long periods and is transformed quantitatively into a white product of the same composition, $[PCl_4]^+F^-$. The ionic nature of this isomer is shown by its solubility and conductivity in methyl cyanide [47].

Similar relationships exist in the following: [48,49]

$$PBr_2F_3 \longleftrightarrow [PBr_4]^+[PF_6]^-, \text{ and}$$

$$PBr_4F \longleftrightarrow [PBr_4]^+F^-.$$

Effect of substituent groups R on the properties of R_nMHal_{5-n} Compounds

It has recently been shown that the properties of the substituted pentahalides R_nMHal_{5-n} are dependent on the nature of the organic group R. Thus, from conductometric studies in methyl cyanide solutions of some of the dihalides of tri-p-tolylarsine, triphenylarsine and tri-p-chlorophenylarsine, Harris and Inglis [50] have drawn attention to a correlation between the electronegativity of the aryl group and the molar conductances of the compounds. They have shown that the molar conductance increases with the decrease in the electronegativity of the substituent aryl group i.e. tri-p-chlorophenylarsine dihalides are weaker electrolytes than triphenyl and tri-p-tolylarsine dihalides. It has been suggested that ionisation of

an R_3PHal_2 molecule involves ionisation of one of the apical P-Hal bonds [51]. Thus it would seem that this becomes easier when the groups attached to the central atom are less electronegative.

Closely correlated with this suggestion are the results of a vibrational spectral studies of $Me_n PF_{5-n}$ made by Schmutzler and Downs [43]. They conclude from the calculated bond orders of the axial P-F bonds that the introduction of much less electronegative methyl group in PF_5 molecule causes a marked weakening of the axial P-F bonds. Conductometric measurements of these fluorophosphoranes in methyl cyanide solutions are entirely consistent with the above observations [52].

Also in keeping with these ideas, it is worth noting that while $Me_n PF_{5-n}$ compounds are exclusively molecular in nature, the analogous chlorophosphoranes $Me_n PCl_{5-n}$ are known to be ionic salts $[Me_n PCl_{4-n}]^+Cl^-$ [53].

It was thought therefore of considerable interest to examine the reactions and products of the reactions of halogens and interhalogens with other tertiary phosphines, arsines and stibines containing strongly electronegative and electropositive substituents; to find out if their properties follow the general pattern outlined for the phosphorus (V) halides derivatives. The work described in this thesis is an investigation of compounds of this type. Tris(pentafluorophenyl) and tris(dimethylamino) derivatives were selected because of the strong electronegative and electropositive nature of their substituent groups respectively. This

work was undertaken to produce a series of their dihalides R_3MHal_2 and tetrahalides R_3MHal_4, analogous to the well known Ph_3MHal_2 and Ph_3MHal_4, for comparative conductance studies, and in order to observe to what extent the course of reaction, and the stability of the adducts formed, was dependent on the nature of the substituent group. The results of this investigation are reported and discussed in part II and III of this thesis.

Studies by Harris and co-workers on halogen adducts of R_3M have so far almost exclusively concerned the halogens bromine, iodine and iodine bromide. Chlorine-containing halogen adducts of triphenylphosphine, arsine and stibine have not been well studied and it was therefore one of the aims of the present work to extend the studies in this field to include those adducts (part I of this thesis).

Some of the findings made in this work have been published in the following papers:

1. Triphenylphosphine - Halogen Adducts of Novel Stoicheiometry.
   M.F. Ali and G.S. Harris; Chem. Comm., 1966, 819.
2. The Structure of Triphenylphosphine Dihalides in Solution.
   G.S. Harris and M.F. Ali; Tetrahedron Letters, 1968, 37-38.
3. The Reactions of Tris(pentafluorophenyl)Phosphine and -Arsine with Halogens and Interhalogens.
   G.S. Harris and M.F. Ali; Inorg. Nucl. Chem. Letters, 4, 5-8 (1968).

PART I

CHLORINE - CONTAINING HALOGEN ADDUCTS OF TRIPHENYLPHOSPHINE, -ARSINE, AND -STIBINE.

I N D E X

INTRODUCTION

Triphenyl derivatives of phosphorus, arsenic, antimony, and bismuth react under certain conditions with halogens and interhalogens giving products of composition Ph_3MHal_2, and in some cases Ph_3MHal_4. A systematic study of these compounds has been made recently by Harris and co-workers.[25,26] From detailed conductance studies they have shown that triphenylphosphorus and -arsenic dihalides are, respectively, strong and weak electrolytes in methyl cyanide; whereas the dihalides of triphenylstibine and -bismuth are non-electrolytes. It has, therefore, been suggested that the tendency towards covalency in Ph_3MHal_2 increases with increasing atomic number of the group V B elements.

The tetrahalides, Ph_3MHal_4, have been obtained as crystalline solids by the addition of halogen to the dihalides in methyl cyanide,

$$Ph_3MHal_2 + Hal_2 = Ph_3MHal_4$$

and the course of halogen addition has been shown to be dependent on the nature of the dihalides themselves. For example, the dihalides of triphenylphosphorus and triphenylarsenic take up an additional molecule of halogen readily,

e.g. $$Ph_3PI_2 + I_2 \longrightarrow Ph_3PI_4$$

$$Ph_3AsBr_2 + Br_2 \longrightarrow Ph_3AsBr_4,$$

and it has been possible to prepare mixed tetrahalides, $Ph_3PBr_nI_{4-n}$ and $Ph_3AsBr_nI_{4-n}$ by reactions such as

$$Ph_3PI_2 + IBr \longrightarrow Ph_3PBrI_3$$

$$Ph_3As + 2IBr \longrightarrow Ph_3AsI_2Br_2.$$

Tetrahalides of triphenylstibine and bismuth have not yet been obtained as crystalline solids, although Ph_3SbI_4 and Ph_3SbBrI_3 have been detected in solution by studying the reactions:

$$Ph_3Sb + 2I_2 \longrightarrow Ph_3SbI^+I_3^-$$

and

$$Ph_3SbI_2 + IBr \longrightarrow Ph_3SbBr^+I_3^-,$$

by conductometric titration.

In the tetrahalides containing only one kind of halogen it has been shown by conductance measurements and the ultraviolet spectrum of their methyl cyanide solution, that trihalide ions are present, arising from the ionisation[25]

$$Ph_3MHal_4 \rightleftharpoons Ph_3MHal^+ + Hal_3^-.$$

The case of the mixed halogen tetrahalides is of particular interest since two ionisation schemes are possible, e.g.

$$Ph_3M(IBr)_2 \rightleftharpoons \begin{cases} Ph_3MI^+ + IBr_2^- & .....(1) \\ Ph_3MBr^+ + I_2Br^- & .....(2) \end{cases}$$

Again from a study of the ultraviolet spectrum of methyl cyanide solutions of this compound, it has been shown that the second ionisation takes place. Without exception, the evidence so far points to the empirical rule that in the mixed tetrahalides, the cation contains the halogen of lower atomic number. For example in the triphenylphosphorus bromide iodides the ions are as follows:

$$Ph_3PIBr_3 \rightleftharpoons Ph_3PBr^+ IBr_2^-$$

$$Ph_3PI_2Br_2 \rightleftharpoons Ph_3PBr^+ I_2Br^-$$

$$Ph_3PI_3Br \rightleftharpoons Ph_3PBr^+ I_3^-.$$

So far, investigations on chlorine-containing halogen adducts of triphenylphosphine, -arsine, and -stibine are limited to the reactions of a few halogens (I_2, Br_2, IBr and ICl) with triphenylarsenic dichloride.[71] Conductometric titrations in these triphenylarsenic dichloride-halogen systems were interpreted as indicating the formation of highly conducting triphenylarsonium tetrahalides (e.g. $Ph_3AsCl_2I_2$, presumed to be $Ph_3AsCl^+ I_2Cl^-$). The crystalline compounds isolated, however, were reported to be tetraphenylarsonium trihalides, and in explanation of this observation it was suggested that the $[Ph_3AsCl]^+$ ion was unstable in a crystal lattice, rearrangement by rapid phenyl migration was assumed to occur, producing Ph_4As^+ in part, and the trihalides of this ion were obtained as solids.

$$2[Ph_3AsCl]^+ \rightleftharpoons Ph_4As^+ + [Ph_2AsCl_2]^+ \qquad \text{.....(3)}$$

In contrast to this reported instability of $[Ph_3AsCl]^+$, triphenylarsenic dichloride is known to react with mercuric chloride to form the addition compound $(Ph_3AsCl_2)_2HgCl_2$. The ionic structure $[Ph_3AsCl]_2^+ [HgCl_4]^{2-}$ was proposed for this compound on the basis of its insolubility in non-polar solvents, its high melting point and its electrical conductivity in methyl cyanide solution.[72] Therefore, the disproportionation of chlorotriphenylarsonium ion as suggested in equation (3) would seem to be very doubtful.

It was thought of great value to undertake a wider investigation of the reactions of Ph_3MCl_2 (M = P, As, Sb) with halogens and interhalogens in an attempt to produce a series of compounds, $Ph_3MCl_nHal_{4-n}$, analogous

to the compounds $Ph_3MBr_nI_{4-n}$, which could be used for comparative conductance studies and to obtain a clearer picture of the nature of the chlorotriphenyl-'onium ion, $[Ph_3MCl]^+$. In the following work two types of reactions leading to chlorine-containing adducts of Ph_3M were studied. These were:

(A) Reactions of Ph_3M (M = P, As, or Sb) with iodine monochloride and iodine trichloride.

(B) Reactions of Ph_3MCl_2 (M = P, As, or Sb) with some halogens (Br_2 or I_2) and interhalogens (IBr, ICl, ICl_3).

RESULTS AND DISCUSSIONS

A. REACTIONS OF Ph_3M WITH IODINE CHLORIDE AND IODINE TRICHLORIDE.

(1) The Reaction of Triphenylphosphine with Iodine Chloride.

The reaction of triphenylphosphine and iodine chloride was studied by conductometric titration and the results of this investigation are recorded in Table (2) and illustrated graphically in Figure [1].

Since triphenylphosphine is virtually a non-conductor, and iodine chloride a very weak electrolyte in methyl cyanide,

$$Ph_3M,\ \Lambda_m = 0.25\ ohm^{-1}\ cm^2\ mole^{-1};\quad c_m = .015\ mole/l$$

$$ICl,\ \Lambda_m = 2.03\ ohm^{-1}\ cm^2\ mole^{-1};\quad c_m = .011\ mole/l;$$

it is quite evident from the results that the interaction of triphenylphosphine and iodine chloride is accompanied by the formation of ions. However, the form of the graph (Fig. 1) with its inflections at mole ratios (iodine chloride: triphenylphosphine) about 0.66:1 and 1.33:1 was very unexpected. The section A-B shows a steep rise in the conductance up to point B which corresponds to a mole ratio of $3Ph_3P:2ICl$. The solution was pale yellow during this stage of the titration. Further addition of iodine chloride (B-C on the graph) led to the appearance of a red colour in the solution and a gradual fall in conductance until the mole ratio $3Ph_3P:4ICl$, after which (C-D), there was a gradual rise in conductance together with an intensification of the colour of the solution.

The ultraviolet and visible spectra of the solution were recorded at different compositions during the conductometric titration and the results are set out in Table (3).

Table 2. Conductometric Analysis of the System Triphenylphosphine - Iodine chloride.

Mole ratio ICl/Ph_3P	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole ratio ICl/Ph_3P	$K \times 10^4$ ohm^{-1} cm^{-1}
0.00	0.002	1.25	3.95
0.15	1.80	1.38	3.40
0.25	2.55	1.53	3.34
0.51	4.10	1.79	3.44
0.62	4.55	2.04	3.62
0.70	5.06	2.29	3.98
0.77	5.00	2.55	4.28
0.90	4.81	2.81	5.00
1.02	4.55	3.06	5.70

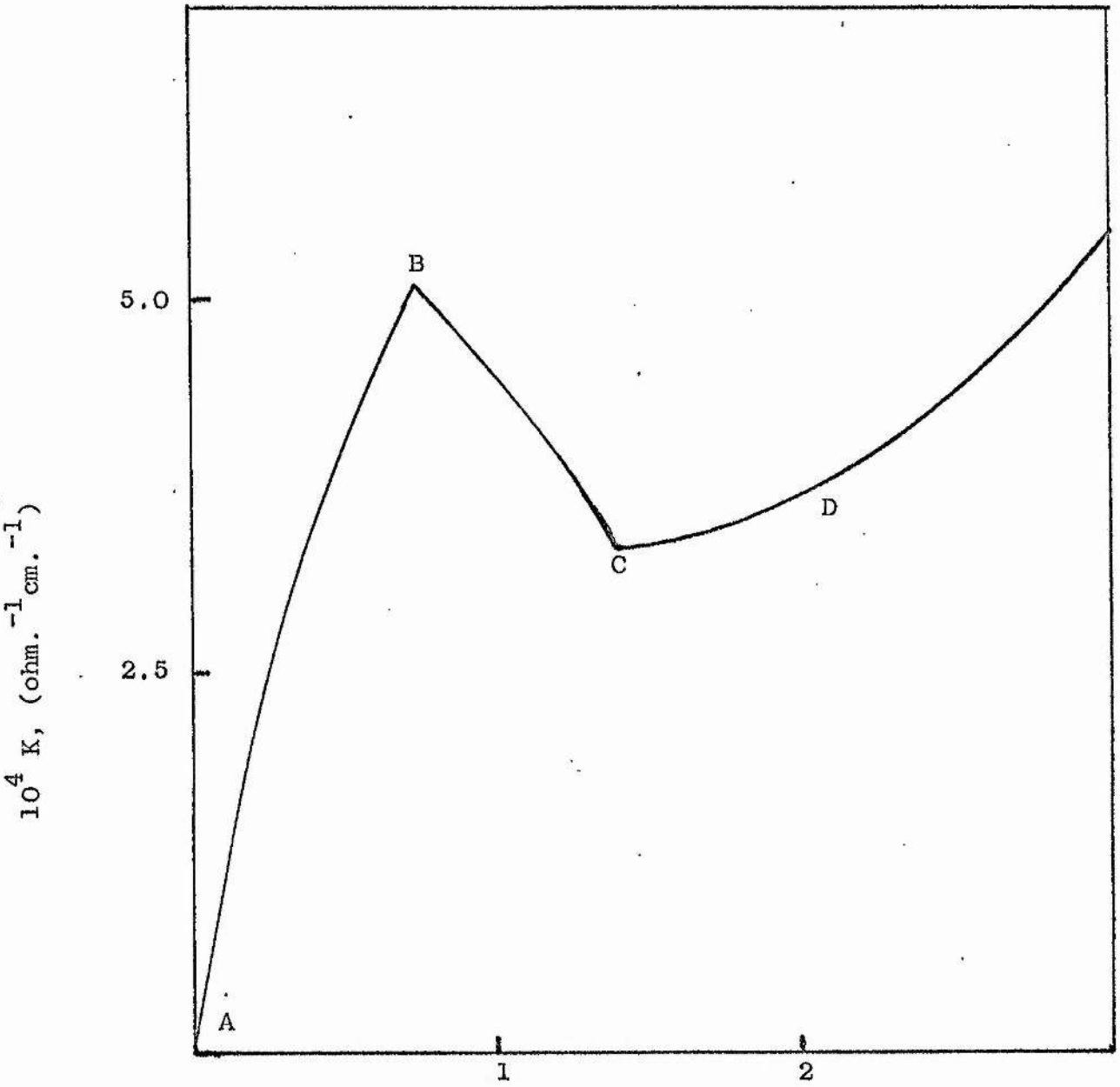


Fig. 1. Conductometric Analysis of the System Triphenylphosphine-Iodine chloride

Table 3. Solution Spectra of the System Triphenylphosphine - Iodine chloride.

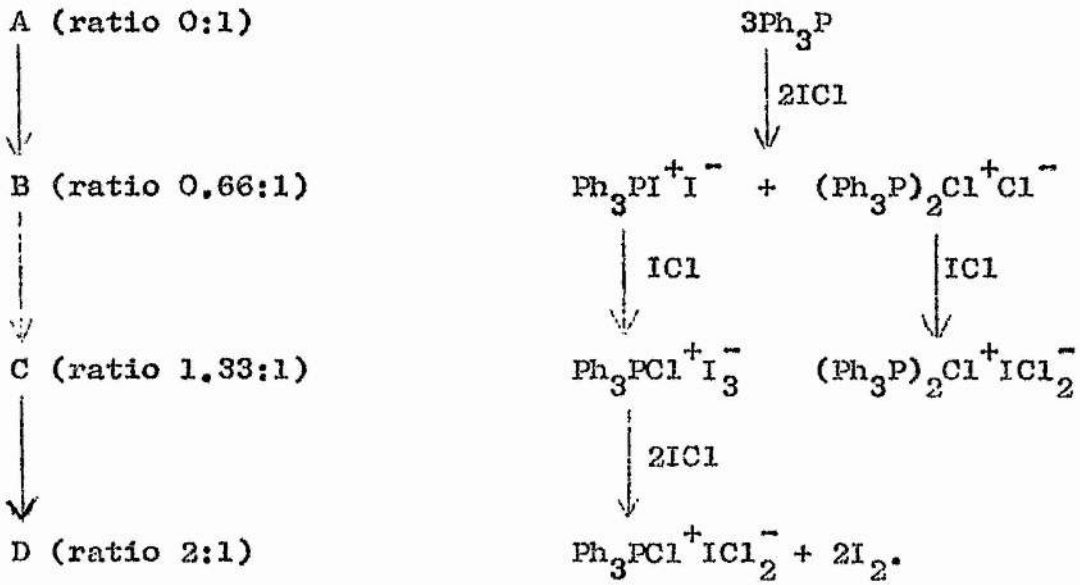
Mole ratio ICl/Ph_3P	UV maxima* (mμ)	UV indicated	Visible maxima (mμ)	Visible indicated
0.4	-	-	-	-
0.6	-	-	-	-
0.8	362,292	I_3^-	-	-
1.0	362,292	I_3^-	-	-
1.5	362,292, 227	I_3^-, ICl_2^-	462	I_2
2.0	227,236	ICl_2^-	462	I_2

*In addition to the peaks shown, the characteristic absorptions of phenylphosphorus (V) compounds were observed at 262, 266 and 273 mμ.[73]

This shows that the tri-iodide ion absorption, which is initially absent (A to B), increases progressively from the conductance maximum to the conductance minimum (B to C), and drops to zero again at 2:1 mole ratio of ICl:Ph_3P.

Triphenylphosphorus di-iodide was isolated from the solution at the 0.5:1 mole ratio, and a compound of novel stoicheiometry, $Ph_3PCl_{0.5}I_{1.5}$, isolated when ether was added to methyl cyanide containing equimolar quantities of iodine chloride and triphenylphosphine. The UV spectrum of a methyl cyanide solution of the compound $Ph_3PCl_{0.5}I_{1.5}$ shows strong tri-iodide ion absorption and its molar conductance in methyl cyanide solution is high, suggesting that the above formula should be doubled and written as the ionic structure, $[(Ph_3P)_2Cl]^+ I_3^-$.

To explain these facts we postulate the following set of reactions in solution:



The precipitation of $(Ph_3P)_2Cl^+ I_3^-$ at 1:1 can be attributed to its low solubility in ether. The compound, $Ph_3PBr_{0.5}I_{1.5}$, believed to have a similar constitution, has been isolated from the reaction of triphenylphosphine and iodine bromide in methyl cyanide.[26]

Although our attempts to isolate $(Ph_3P)_2Cl^+Cl^-$ were not successful, evidence for its formation was obtained by conductometric study, by cryoscopic determination of molecular weight, and by the isolation of other compounds containing a $(Ph_3P)_2Hal^+$ cation, as follows:

(a) Conductometric study: Since triphenylphosphorus dichloride ionises in methyl cyanide thus:

$$Ph_3PCl_2 \rightleftharpoons Ph_3PCl^+ + Cl^-$$

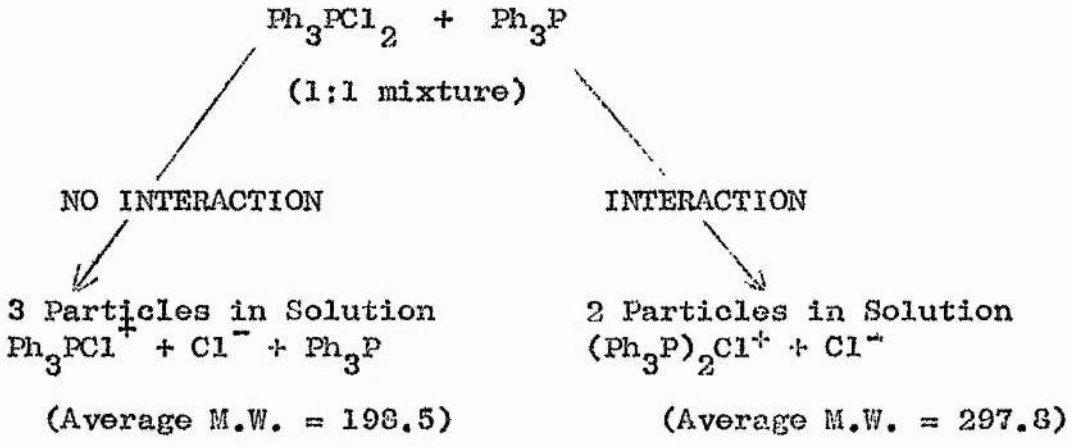
it was thought that addition of triphenylphosphine to such a solution ought to result in the formation of the postulated compound $(Ph_3P)_2Cl^+Cl^-$

$$Ph_3PCl^+ Cl^- + Ph_3P \longrightarrow (Ph_3P)_2Cl^+Cl^-.$$

Furthermore, if this reaction does occur it seemed reasonable to expect that it might be shown up in a conductometric titration of the reactants.

Addition of triphenylphosphine to a methyl cyanide solution of triphenylphosphorus dichloride resulted in a uniform increase in the conductance of the solution until the 1:1 mole ratio was reached at which point there was a marked change in gradient. The break in the graph along with the high molar conductance of the solution at this point (Λ_m = 60.6 ohm^{-1} cm^2 mole^{-1} at c_m = .017 mole/l) was taken as good evidence for the presence of a new conducting species, of composition $(Ph_3P)_2Cl^+Cl^-$, in solution.

(b) Cryoscopic Study: Molecular weight determinations were made in nitrobenzene solutions containing a 1:1 mixture of triphenylphosphorus dichloride and triphenylphosphine to provide evidence for the interaction of these two compounds:



Several estimations were made at different concentrations and the mean value obtained for the molecular weight of the solute was 297.0, which is remarkably close to that expected if interaction occurs in the manner postulated.

(c) Compounds containing $(Ph_3P)_2Hal^+$ cations:

In addition to $(Ph_3P)_2Cl^+ I_3^-$ and $(Ph_3P)_2Br^+ I_3^-$, which have already been mentioned, it has been possible to isolate one other compound which appears to contain a $(Ph_3P)_2Hal^+$ - type of ion. When ether was added to an equimolar mixture of $(Ph_3P)_2HgBr_2$ and bromine in methyl cyanide a white solid was precipitated, analysis of which indicated the composition $(Ph_3P)_2HgBr_4$. From its properties it appeared that this compound should be formulated, $(Ph_3P)_2Br^+ HgBr_3^-$.

Some properties of these three compounds are summarised along with those of the triphenylphosphorus dihalides in Table 4.

Table 4. Crystalline Adducts containing the $[(Ph_3P)_2Hal]^+$ ion.

Compound	Colour	m.p. °C	M.W. (obs.)	M.W./2 (calc.)	Λ_m ohm^{-1} cm^2 mole^{-1} at 25°; c_m = .01	IR Spectra ν P-Hal(cm^{-1})
$(Ph_3P)_2Cl^+ I_3^-$	yellow	218	481.7	470.4	127.2	P-Cl, 580
$(Ph_3P)_2Br^+ I_3^-$	yellow	244-245	497.0	492.6	95.0	P-Br, 490
$(Ph_3P)_2Br^+ HgBr_3^-$	white	130	513.9	522.3	117.5	P-Br, 490
Ph_3PCl_2	-	-	-	-	78.1	P-Cl, 580
Ph_3PBr_2	-	-	-	-	73.2	P-Br, 490

The unexpected ion-type $[(Ph_3P)_2Hal]^+$ has not to our knowledge been reported previously, and regarding its structure, there would seem to be two possibilities:

$$[Ph_3P \rightarrow Hal \leftarrow PPh_3]^+ \qquad \text{or} \qquad [Ph_3P - \underset{Hal}{|} - PPh_3]^+$$

[A] [B]

Structure [A]. This structure is analogous to that of the cation in the well known positive iodine compounds, e.g.

$$[py \longrightarrow I \leftarrow Py]^+ ClO_4^-.$$ [74]

Structure [B]. This structure may be considered to be derived from the compound type Ph_3P(Hal)—(Hal)PPh_3. Only one example of such a compound has been reported,[75] namely Ph_3P(Br)—(Br)PPh_3, which is obtained from the reaction of cyanogen bromide and triphenylphosphine in the absence of solvent.

Although the co-ordinated iodine cation is relatively stable and is present in a number of compounds, the corresponding bromine and chlorine cations in the +1 oxidation state are reported to be quite unstable.[76] In a bridged structure such as that present in [A], the P-Hal stretching frequency would be expected to occur at a lower frequency than in an unbridged system (e.g. in Ph_3PCl_2). The aluminium trichloride dimer, for example, has its terminal ν Al-Cl at 625cm^{-1} whereas the bridged ν Al-Cl is at 420cm^{-1}.[77a] In the present case the bands attributed to the P-Hal stretching frequency in the infra-red spectra of the compounds (Table 3) lie close to the frequencies expected for non-bridging P-Hal bands, and in fact lie at the upper end of the range of frequencies usually quoted for P-Br and P-Cl stretching vibrations.

The evidence therefore supports structure [B] for the ion $[(Ph_3P)_2HaI]^+$. The P-P stretching frequency in these ions should lie in the range 600-350cm^{-1},[77b] but owing to the strong P-C vibrations in this region we were not able to assign this vibration.

(2) Reaction of Triphenylphosphine with Iodine Trichloride.

Conductometric titration of triphenylphosphine with iodine trichloride in methyl cyanide gave the results shown in Table (5), and Figure (2).

Table 5. Conductometric Analysis of the System Triphenylphosphine - Iodine Trichloride

Mole ratio ICl_3/Ph_3P	$K \times 10^4$ $ohm^{-1}cm^{-1}$	Mole ratio ICl_3/Ph_3P	$K \times 10^4$ $ohm^{-1}cm^{-1}$
0.00	0.003	0.73	1.82
0.07	0.69	0.78	2.00
0.16	1.36	0.87	2.52
0.24	1.78	0.96	3.30
0.33	2.16	1.00	3.44
0.48	2.50	1.05	3.66
0.56	1.89	1.13	3.84
0.60	1.38	1.22	3.84
0.64	1.37	1.31	3.83
0.69	1.57	1.49	3.81

The shape of the conductance graph again indicates that the reaction is not a simple one. From the beginning until the 0.5:1 ratio ($ICl_3:Ph_3P$) there is a steep rise in specific conductance and during this stage the solution was pale yellow in colour. Further additions of ICl_3 produced a deep-red solution and a lowering of the conductance

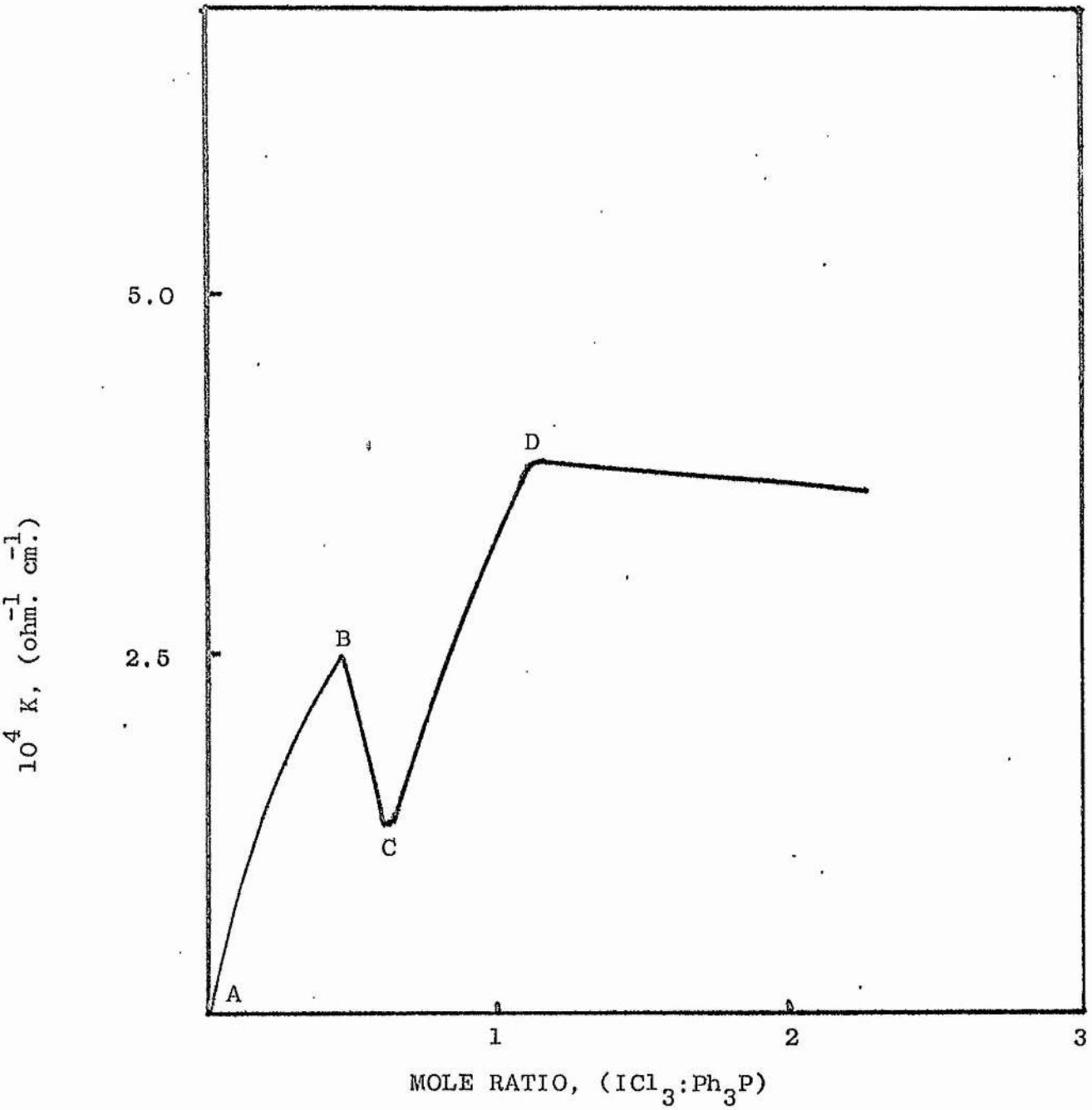


Fig. 2. Conductometric Analysis of the System Triphenylphosphine-Iodine trichloride

until the point C (mole ratio ca. 0.75:1) was attained, whereupon the conductance rose sharply and the colour of the solution became yellow once more. A marked inflection occurred at the 1:1 ratio. The molar conductance values calculated for the solution at 0.5:1 and 1:1 mole ratios are respectively:

$$\Lambda_m = 59.0 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1} \ (c_m = 0.0045 \text{ mole/l})$$

$$\Lambda_m = 85.0 \text{ ohm}^{-1}\text{cm}^2 \text{ mole}^{-1} \ (c_m = 0.0040 \text{ mole/l}).$$

Ultraviolet and visible spectra of the solutions with respect to different portions of the graph gave the following results (Table 5).

Table 5. Solution Spectra of the system Triphenylphosphine - Iodine trichloride.

Conductance Graph	Colour of the Solution	UV indicates
A - B	yellow	-
B - C	red	I_3^-, I_2
C - D	red	I_3^-, I_2, ICl_2^-
D	yellow	ICl_2^-

The reaction of ICl_3 with Ph_3P seems to occur in three distinct stages, the first being the formation of the dihalides, Ph_3PICl and Ph_3PCl_2 at the 0.5:1 (ICl_3:Ph_3P) mole ratio.

$$2\ Ph_3P + ICl_3 \longrightarrow Ph_3PICl + Ph_3PCl_2 \qquad \ldots\ldots\ldots(4)$$

Solid Ph_3PICl was in fact isolated from the solution at this ratio. It is perhaps not surprising that the first stage of the reaction should follow this course because it is well known that in solution iodine

trichloride readily dissociates into iodine chloride and chlorine.[73].

In the second stage of the reaction (B - C) the Ph_3PICl formed in the first stage is converted into Ph_3PCl_2,

$$Ph_3PICl + \frac{1}{3} ICl_3 \longrightarrow Ph_3PCl_2 + \frac{2}{3} I_2, \quad \text{.....(5)}$$

so that all of the original Ph_3P is now present as Ph_3PCl_2. The production of iodine accords with the observed changes in colour and U.V. spectrum.

In the third stage the Ph_3PCl_2 is converted to the tetrahalide Ph_3PCl_3I ($\equiv Ph_3PCl^+ICl_2^-$) thus

$$2\ Ph_3PCl_2 + (\frac{2}{3} I_2 + \frac{2}{3} ICl_3) \longrightarrow 2\ Ph_3PCl_3I \quad \text{.....(6)}$$

$$\equiv 2\ ICl.$$

Again, the colour changes are in accord with this reaction and the steep rise in conductance from C to D corresponds to the formation of the tetrahalide Ph_3PCl_3I ($Ph_3PCl^+\ ICl_2^-$) which is a strong electrolyte in methyl cyanide.

Summing equations (4), (5), and (6) gives the overall reaction to the 1:1 ratio:

$$2\ Ph_3P + 2\ ICl_3 \longrightarrow 2\ Ph_3PCl_3I.$$

As mentioned earlier, triphenylphosphorus chloride iodide was readily obtained as a yellow crystalline solid at the 0.5:1 ratio. The tetrahalide, Ph_3PCl_3I, was isolated at the 1:1 mole ratio. The molar conductances of these adducts determined at 25°C were:

Ph_3PClI —— $\Lambda_m = 67.6\ ohm^{-1}\ cm^2\ mole^{-1}$ ($c_m = .01$ mole/l)

Ph_3PCl_3I —— $\Lambda_m = 114.0\ ohm^{-1}\ cm^2\ mole^{-1}$ ($c_m = .01$ mole/l).

(3) Reaction of Triphenylarsine with Iodine chloride:

The conductance-composition graph for the system triphenylarsine-iodine chloride is reproduced in Figure (3).

The initially colourless solution of triphenylarsine (Λ_m = 0.02 ohm^{-1} cm^2 mole^{-1}; c_m = .0095 mole/1) showed the characteristic dark colouration of trihalide ion from the first addition of iodine chloride and the conductance rose steadily up to the 2:1, ($ICl:Ph_3As$) mole ratio corresponding to the formation of a strong electrolyte of composition $Ph_3AsI_2Cl_2$ (Λ_m = 77.20 ohm^{-1} cm^2 mole^{-1}; c_m = 0.0071 mole/1).

$$Ph_3As + 2ICl \longrightarrow Ph_3AsCl^+I_2Cl^-$$

The ultra violet spectrum of the solution showed that the I_2Cl^- ion* was formed in the titration from the first addition up to the conductance break at the 2:1 ratio. Thereafter (B - C in Figure 3) the I_2Cl^- ion absorptions at 365 mμ and 290 mμ gradually disappeared and the U.V. and visible spectra of the solution showed strong absorptions at 460 mμ (iodine in methyl cyanide solution), and at 338 mμ (ICl_2^- in methyl cyanide). Thus the I_2Cl^- ion is being converted to the more stable ICl_2^- by excess iodine chloride $I_2Cl^- + ICl \longrightarrow ICl_2^- + I_2$. A strong absorption at 227 mμ was also observed, this is mainly due to the phenyl group and masks the I_2Cl^- and ICl_2^- absorptions at this ~~frequency~~ wave length.

*Absorption maxima were observed at 227 mμ, 262 mμ, 290 mμ, and 365 mμ. The absorptions at 290 and 365 mμ are characteristic of I_3^-, and the one at 227 mμ of ICl_2^-, suggesting a ready dissociation of I_2Cl^- in methyl cyanide ($2I_2Cl^- \rightleftharpoons I_3^- + ICl_2^-$). The absorption at 262 mμ is due to I_2Cl^-. [79]

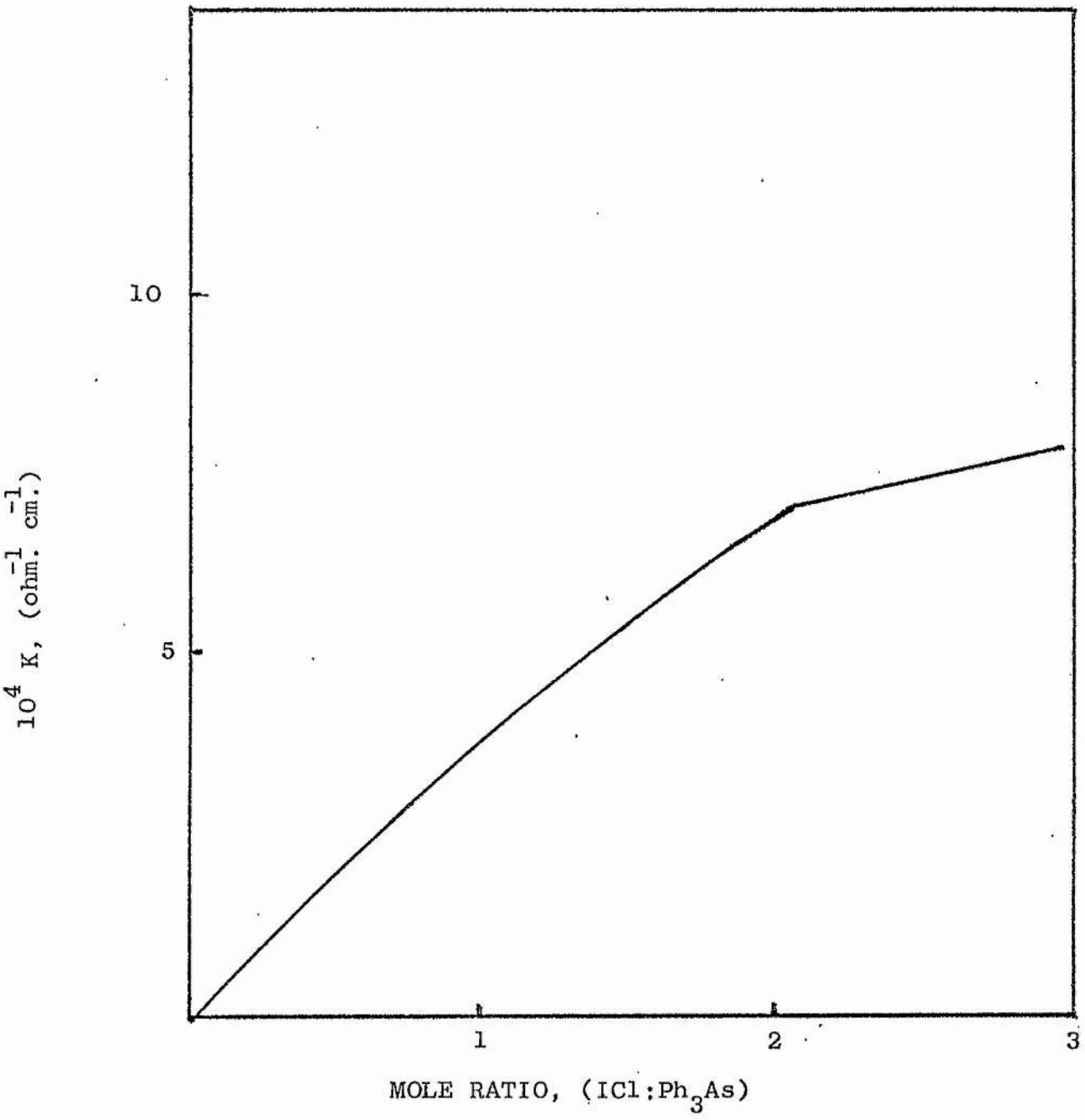


Fig.3. Conductometric Analysis of the System Triphenylarsine-Iodine chloride

This reaction is therefore similar to the reaction of triphenylarsine with iodine bromide and the overall reaction can be explained by the following scheme.

A to B (ratio 2.0) $Ph_3As + 2\ I\ Cl \rightleftharpoons Ph_3AsCl^+ + I_2Cl^-$ .....(7)

B to C (ratio 3.0) $I_2Cl^- + ICl \longrightarrow ICl_2^- + I_2$ .....(8)

To confirm that reaction (8) is a general one, a spectrophotometric study of the reaction of tetraphenylarsonium di-iodochloride and iodine chloride in methyl cyanide was made; this showed quite clearly the replacement of the absorptions characteristic of I_2Cl^- with those characteristic of ICl_2^-.

$$Ph_4As^+I_2Cl^- \xrightarrow{ICl} Ph_4As^+ICl_2^- + I_2.$$

A number of attempts were made to isolate the tetrahalide $Ph_3AsI_2Cl_2$ from the reaction of stoicheiometric quantities of triphenylarsine and iodine chloride in methyl cyanide. A dark brown solid was obtained by evaporation of the solvent but on analysis this gave a high value for iodine. Recrystallization from organic solvents failed to yield the pure compound. This, it is thought, is due to the disporportionation of the unstable I_2Cl^- ion ($\longrightarrow I_2 + Cl^-$). This, as has already been mentioned, occurs to some extent in methyl cyanide[79] and it is likely that the solid isolated is the tetrahalide contaminated with iodine.

(4) Reaction of Triphenylarsine with Iodine trichloride:

The triphenylarsenic dichloride - iodine chloride system has been studied in some detail by A.D. Beveridge who reported that a 1:1 addition compound (Ph_3AsCl_3I) could not be isolated, although its existence in methyl cyanide was shown by conductometric titration.[71] A possible alternative approach to this adduct was thought to be the reaction of triphenylarsine with iodine trichloride.

$$Ph_3As + ICl_3 \longrightarrow Ph_3AsCl_3I$$

Conductometric titration of Ph_3As with ICl_3 in methyl cyanide was therefore carried out and this gave the results shown in Table (7) and Figure (4).

Table 7. Conductometric Analysis of the System Triphenylarsine - Iodine trichloride

Mole ratio ICl_3/Ph_3As	$K \times 10^4$ $ohm^{-1}\ cm^{-1}$	Mole ratio ICl_3/Ph_3As	$K \times 10^4$ $ohm^{-1}\ cm^{-1}$
0.0	.003	1.17	7.60
0.08	0.37	1.25	7.70
0.17	0.63	1.34	7.71
0.33	1.12	1.50	7.74
0.50	1.60	1.67	7.75
0.67	2.34	.33	7.76
0.83	4.08	2.00	7.78
0.92	4.04	2.33	7.80
1.00	5.95	2.67	7.95
1.08	6.95	-	-

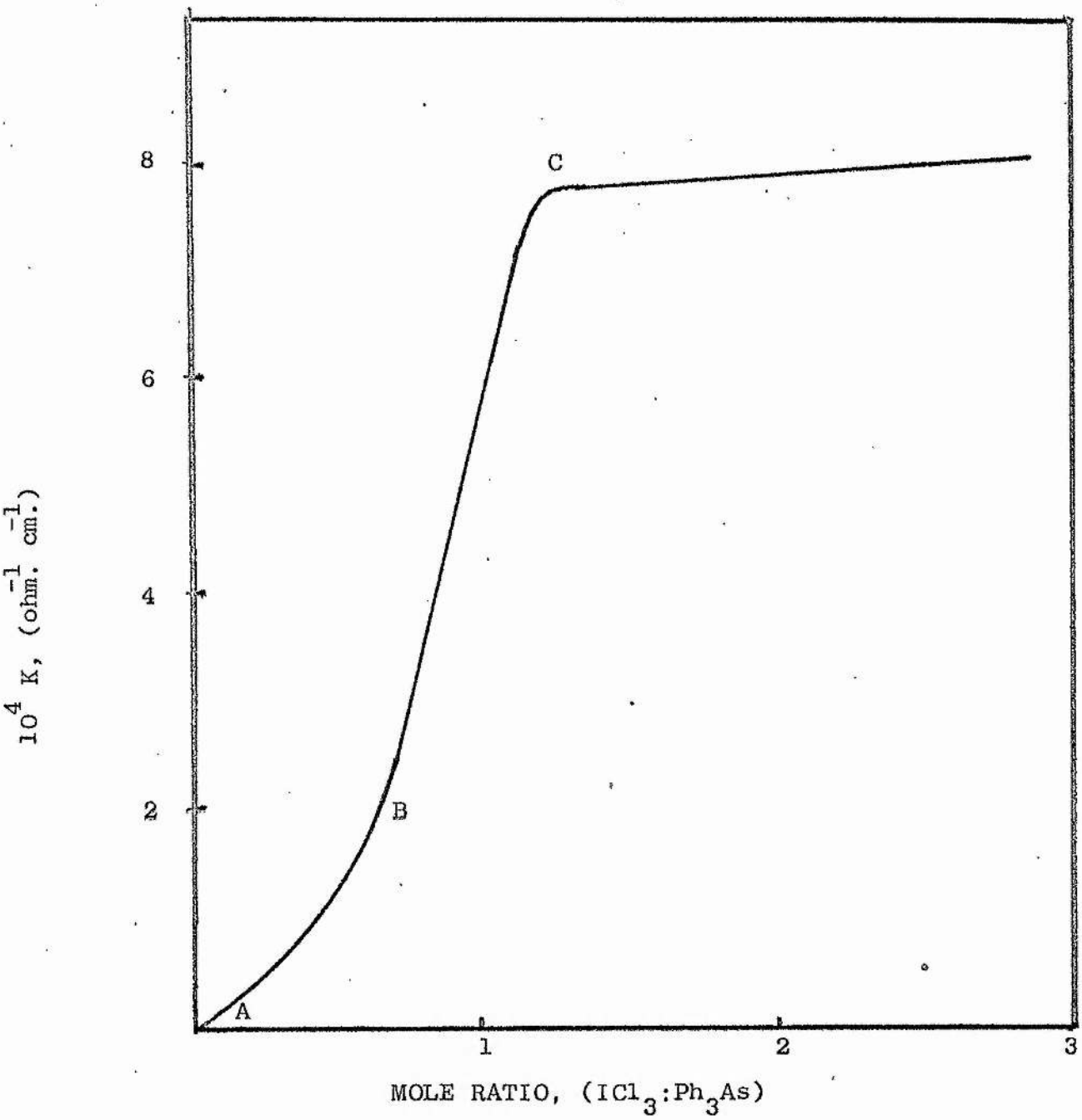


Fig.4. Conductometric Analysis of the System Triphenylarsine-Iodine trichloride

The form of the graph shows that the system is quite different from that of triphenylphosphine-iodine trichloride. The solution was strongly coloured (deep red) from the first addition of iodine trichloride and the conductance rose slowly to a low value at about 0.66:1 (ICl_3:Ph_3As) mole ratio (A - B). From the 0.66:1 to the 1:1 mole ratio (B - C) the solution gradually acquired an intense yellow colour and the conductance rose rapidly. Thereafter the conductance rose only slowly thus giving a break at the 1:1 mole ratio; at this ratio, Λ_m = 93.50 ohm^{-1} cm^2 $mole^{-1}$ (c_m = .0064 mole/l).

A spectrophotometric study of the reaction in methyl cyanide showed the presence of iodine and I_2Cl^- from the first addition of iodine trichloride solution up to point B when the concentration of iodine reached its maximum. On further addition of iodine trichloride (B - C) the absorption at 460 mμ (due to I_2) gradually disappeared and a new peak appeared at 338 mμ. This latter peak is characteristic of ICl_2^- ion; the 227 mμ peak of ICl_2^- was masked by the phenyl peak at that frequency.

The conductance and U.V. results can be readily interpreted according to the following scheme:

$$A \longrightarrow B \quad 3\ Ph_3As + 2\ ICl_3 \longrightarrow \underbrace{3\ Ph_3AsCl_2 + I_2}$$

$$\downarrow\uparrow$$

$$2\ Ph_3AsCl_2 + Ph_3AsCl^+\ I_2Cl^-$$

$$B \longrightarrow C \quad 3\ Ph_3AsCl_2 + I_2 + ICl_3 \longrightarrow 3\ Ph_3AsCl^+.\ ICl_2^-$$

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overall reaction to 1:1 ratio $\quad 3\ Ph_3As + 3\ ICl_3 \longrightarrow 3\ Ph_3AsCl^+.\ ICl_2^-$

This scheme includes as the end product the anticipated 1:1 adduct, triphenylarsenic trichloride iodide which was isolated as a yellow crystalline solid, m.p. 80-81°, by the addition of anhydrous ether to a 1·1 mixture of Ph_3As and ICl_3 in methyl cyanide. The molar conductance of this adduct at 25° was found to be, Λ_m = 108.0 ohm^{-1} cm^2 $mole^{-1}$ (c_m = .01mole/1.

(5) Reaction of Triphenylstibine with Iodine chloride:

The system triphenylstibine - iodine bromide has been shown to behave quite differently from the corresponding ones involving triphenylphosphine and triphenylarsine, and there is no evidence for the existence of $Ph_3SbI_2Br_2$ in solution.[26] It was therefore of interest to study the reaction of triphenylstibine with iodine chloride for comparison.

The conductance-composition graph (Fig. 5) like that of the Ph_3Sb-IBr system possesses a humped shape and in fact both graphs are very similar with respect to the position of their inflections and maximum. The solution was pale yellow up to $ICl:Ph_3Sb$ = 1:1, and the conductance rose only very slightly from its near zero value as iodine chloride was added up to 1:1 ratio. Thereafter, the solution became deep red and the conductance rose more rapidly to a maximum at the mole ratio ca. 1.5:1, followed by a minimum in the specific conductance at the 2:1 ($ICl:Ph_3Sb$) mole ratio. Molar conductances at the 1:1 and 2:1 mole ratios were respectively:

1:1 Λ_m = 3.07 ohm^{-1} cm^2 $mole^{-1}$ (c_m = .0091 mole/1)

2:1 Λ_m = 6.75 ohm^{-1} cm^2 $mole^{-1}$ (c_m = .0080 mole/1).

Thus the species present in solution at these ratios are virtually non-electrolytes in methyl cyanide.

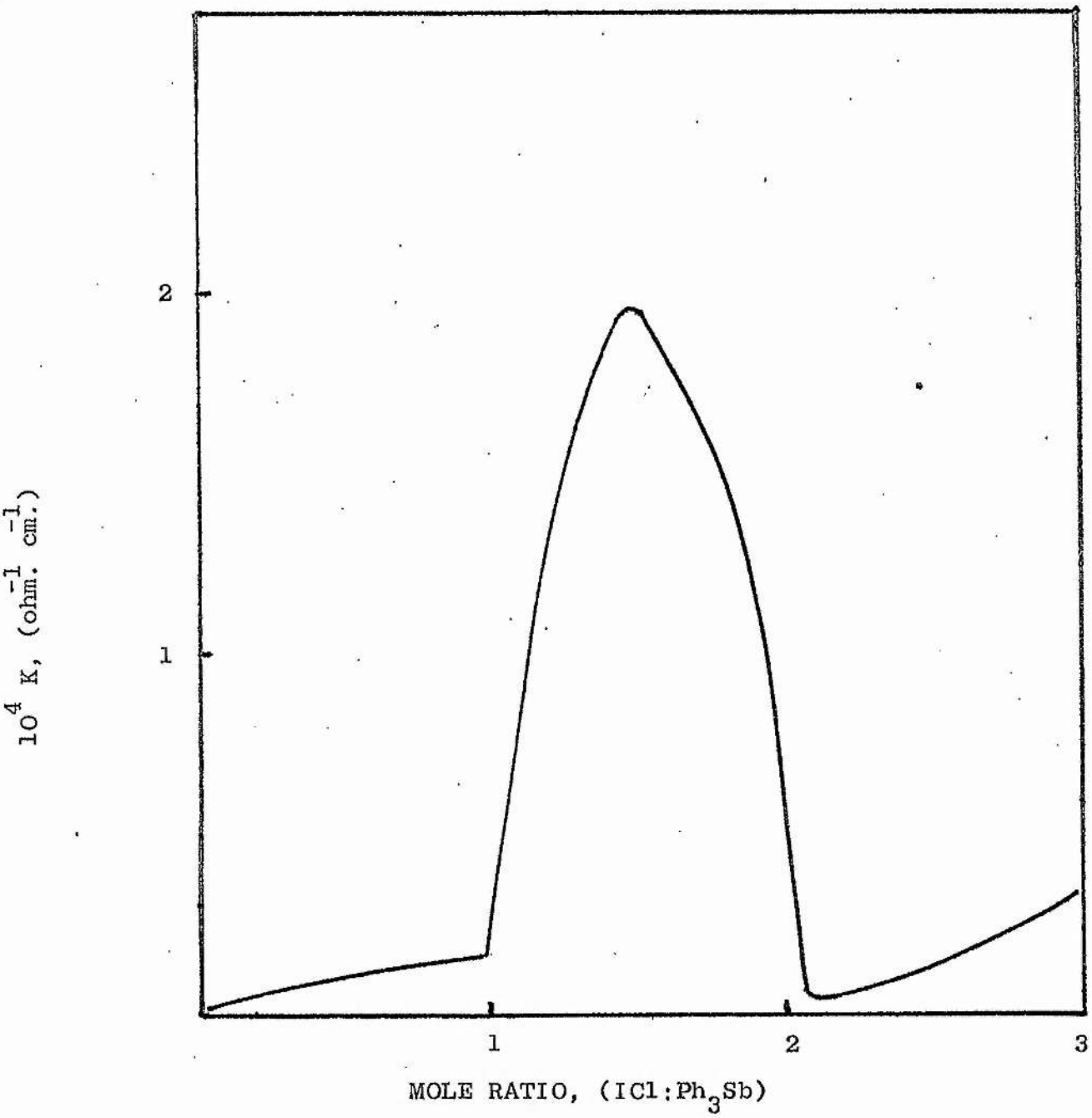


Fig. 5. Conductometric Analysis of the System Triphenylstibine-Iodine chloride

Examination of the ultraviolet spectrum of the solution at different compositions indicated the presence of tri-iodide ion between the 1:1 and 2:1 mole ratios. From the beginning up to the 1:1 ratio and beyond the 2:1 ratio, no I_3^- was present. However from the 2:1 ratio onwards the solution contained molecular iodine.

Therefore, by analogy with Ph_3Sb-IBr system, the conductance and spectral data can be interpreted on the basis of the following reactions occurring.

$$0 - 1{:}1 \quad Ph_3Sb + ICl \longrightarrow Ph_3SbICl \quad .....(9)$$

$$1{:}1 - 2{:}1 \quad Ph_3SbICl + ICl \longrightarrow Ph_3SbCl_2 + I_2 \quad ....(10)$$

Support for this came from the isolation of Ph_3SbICl and Ph_3SbCl_2 from the solution at the 1:1 and 2:1 ratios respectively.

Again by analogy with the Ph_3Sb - IBr system, the strong maximum in the conductance-composition graph can be explained. As reaction (10) proceeds, iodine is formed and this combines temporarily with unreacted Ph_3SbICl to give the tetrahalide, Ph_3SbClI_3:

$$Ph_3SbICl + I_2 \longrightarrow Ph_3SbCl^+ I_3^- \quad .....(11).$$

The extent of the formation of the tetrahalide will be greatest when the overall reaction (10) leading to Ph_3SbCl_2 is half complete, thus accounting for the conductance maximum at the 1.5:1 ($ICl:Ph_3Sb$) mole ratio. Tri-iodide ion absorption in the U.V. is also at a maximum at this ratio.

Evidence for the existence of $Ph_3SbCl^+ I_3^-$ in methyl cyanide was obtained by observing a 1:1 break in the graph of a conductometric titration of Ph_3SbICl with iodine. Attempts to isolate this compound by

the addition of ether to methyl cyanide solutions of Ph_3SbICl and iodine gave a dark red cyrstalline solid, but this contained no chlorine so that it could not be formulated as a tetrahalide. The analytical data (C, 44.53; H, 3.04; I, 25.70%) was however in keeping with the formulation of this compound as $(Ph_3SbI)_2O$ ($C_{36}H_{30}Sb_2I_2O$ requires: C, 44.4; H,3.08; I, 26.0%). Two compounds of this type, namely $(Ph_3SbCl)_2O$ and $(Ph_3SbBr)_2O$ have been prepared recently by Doak et. al. from the partial hydrolysis of triphenyl antimony dihalides, and these authors have shown that the compounds contain an Sb-O-Sb bridge whose stretching vibration gives a broad band at ca. 760 cm^{-1}.[80] The iodine compound isolated in the present work has a band in this region lending further support to its formulation as a $(Ph_3SbHal)_2O$ compound. The formation of this compound could reveal the ingress of sufficient moisture at some stage of the reaction to cause hydrolysis either of the tetrahalide being sought or the reactant Ph_3SbICl.

$$2\ Ph_3SbCl^+\ I_3^- + H_2O \longrightarrow (Ph_3SbI)_2O + 2HCl + 2I_2$$

$$2\ Ph_3SbICl + H_2O \longrightarrow (Ph_3SbI)_2O + 2HCl$$

However since as in all of this work very strict precautions were taken to exclude water at all stages the possibility that the ether is the source of oxygen in the product cannot be excluded;

$$\text{e.g.}\quad 2\ Ph_3SbICl + Et_2O \longrightarrow (Ph_3SbI)_2O + 2EtCl.$$

Reactions of dihalides of this sort with ether are not unknown: for example under certain conditions Ph_3PHal_2 reacts with ether to produce Ph_3PO and Et Hal.[81]

(6) Reaction of Triphenylstibine with Iodine trichloride:

Among the trihalide ions involving chlorine and iodine, ICl_2^- is known to be the most stable, hence the mixed tetrahalide, Ph_3SbCl^+ ICl_2^-, would be expected to be the most favoured of the series $Ph_3SbI_nCl_{4-n}$. To investigate this, the system triphenylstibine-iodine trichloride,

$$Ph_3Sb + ICl_3 \longrightarrow Ph_3SbICl_3 \rightleftharpoons Ph_3SbCl^+ICl_2^- \quad .....(12)$$

was studied by conductometric titration, the results of which are recorded in the Table (8) and shown graphically in Figure (6).

Table 8. Conductometric Analysis of the System Triphenylstibine - Iodine trichloride.

Mole ratio ICl_3/Ph_3Sb	$K \times 10^4$ ohm^{-1} cm^{-1}	Mole ratio ICl_3/Ph_3Sb	$K \times 10^4$ ohm^{-1} cm^{-1}
0.00	0.001	1.14	1.30
0.20	0.09	1.24	1.70
0.38	0.17	1.45	2.20
0.58	0.35	1.65	2.80
0.70	2.30	1.86	3.20
0.82	2.74	2.06	3.50
0.94	1.47	2.20	4.00
1.04	0.73	-	-

The conductance of triphenylstibine solution rose very slightly on the addition of iodine trichloride solution up to the 0.5:1 (ICl_3:Ph_3Sb) mole ratio (A - B), during which the solution was pale yellow in colour. The conductance then rose sharply (B - C), and fell sharply (C - D), giving

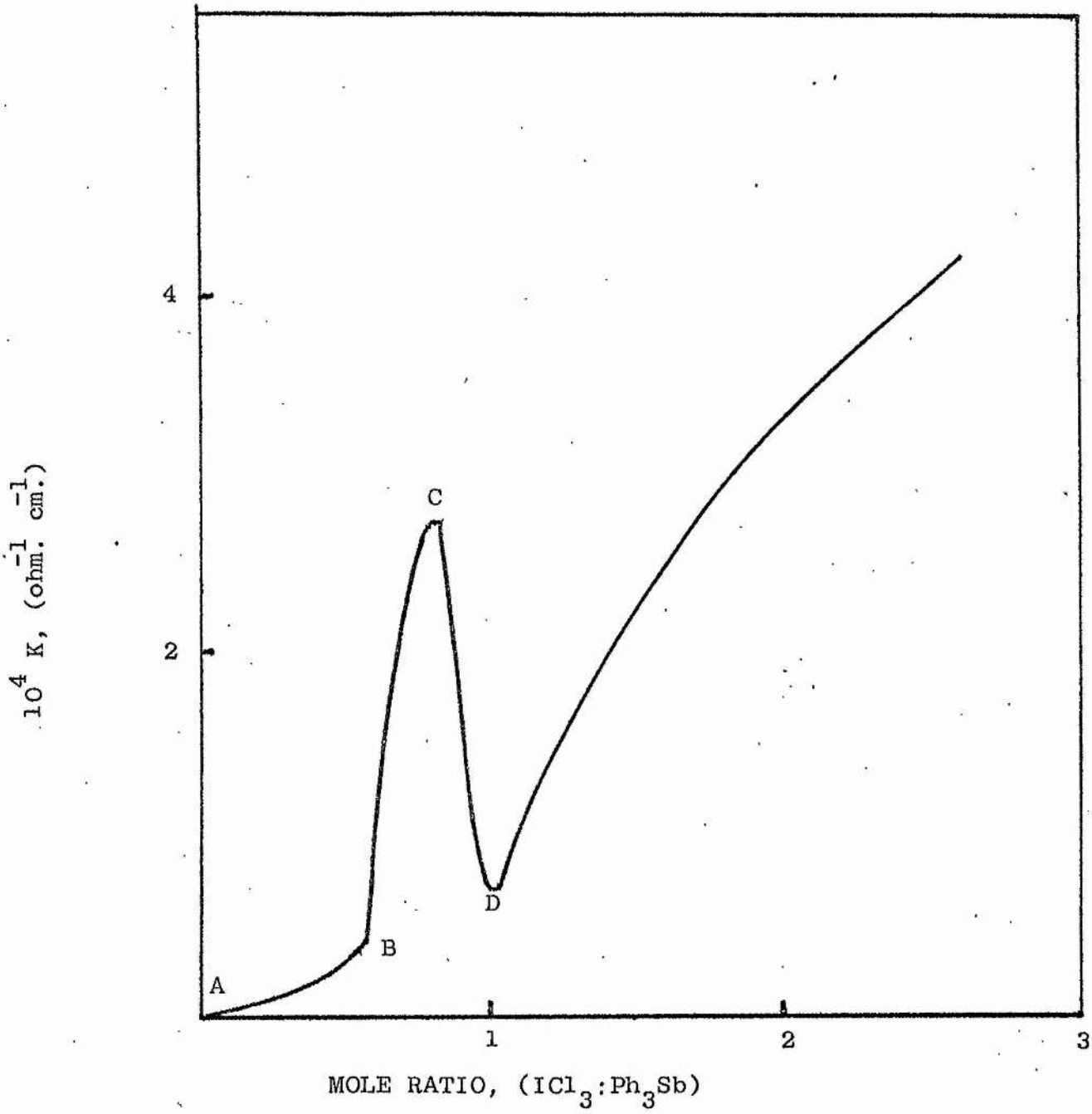


Fig. 6. Conductometric Analysis of the System Triphenylstibine-Iodine trichloride

a distinct maximum between mole ratios 0.5:1 and 1:1. The solution was deep red during this stage (B - D) of titration. After the 1:1 mole ratio the conductance increase was gradual and corresponds to the addition of iodine trichloride to the pure solvent.

Spectrophotometric study of the solution at different stages during the reaction indicated the formation of tri-iodide ion between 0.5:1 and 1:1 ratio.

Ph_3SbICl and Ph_3SbCl_2 were isolated at 0.5:1 and 1:1 (ICl_3:Ph_3Sb) mole ratios respectively. All these facts suggest that the reaction occurring in solution is as follows:

(A - B) $$2\ Ph_3Sb + ICl_3 \longrightarrow Ph_3SbICl + Ph_3SbCl_2 \quad \text{.....(13)}$$

(B - D) $$Ph_3SbICl + ICl_3 \longrightarrow Ph_3SbCl_2 + I_2 + Cl_2 \quad \text{.....(14).}$$

The maximum in this graph can be accounted for as before, if the iodine produced in reaction (14) interacts temporarily with the unreacted Ph_3SbICl to give the tetrahalide, Ph_3SbI_3Cl.

$$Ph_3SbICl + I_2 \longrightarrow Ph_3SbCl^+ I_3^-$$

This secondary interaction will occur to its maximum extent midway between the 0.5:1 and 1:1 mole ratio.

Thus the overall reaction of iodine trichloride and triphenylstibine is to produce the dihalide Ph_3SbCl_2 and not the tetrchalide as envisaged in reaction (12).

B. REACTIONS OF Ph_3MCl_2 (M = P, As and Sb) WITH HALOGENS.

(1) The Structure of Ph_3MCl_2 in solution.

The nature of triphenylarsenic dichloride in solution has been deduced from conductance and electrolysis experiments by Harris and Beveridge.[25] It has been suggested that triphenylarsenic dichloride is a weak electrolyte in methyl cyanide solution, ionising according to the equation;

$$2\ Ph_3AsCl_2 \rightleftharpoons Ph_3AsCl^+ + Ph_3AsCl_3^-.$$

Similarly, the very low molar conductance value for triphenylantimony dichloride ($\Lambda_m < 1$) has been interpreted as indicating that Ph_3SbCl_2 is present in methyl cyanide as essentially covalent species.[26]

Triphenylphosphorus dichloride is a strong 1:1 electrolyte (Λ_m = 73.1 ohm^{-1} cm^2 mole^{-1}; c_m = .01 mole/l), which is probably completely ionised in solution. There are two likely ways in which the ionisation might take place, namely,

$$Ph_3PCl_2 \rightleftharpoons Ph_3PCl^+ + Cl^- \qquad \text{.....(15)}$$

$$2\ Ph_3PCl_2 \rightleftharpoons Ph_3PCl^+ + Ph_3PCl_3^- \qquad \text{.....(16).}$$

The scheme (16), by analogy with the behaviour of phosphorus (v) chloride in methyl cyanide, would seem to be not unlikely. In it the formation of the $Ph_3PCl_3^-$ ion implies the acceptance of a chloride ion by a Ph_3PCl_2 molecule. To investigate this, the reaction of Ph_3PCl_2 with a strong chloride ion donor, Et_4NCl, was examined.

$$Et_4\overset{+}{N}Cl^- + Ph_3PCl_2 \longrightarrow Et_4N^+Ph_3PCl_3^- \qquad \text{.....(17)}$$

The reaction was carried out by stepwise addition of Et_4NCl to Ph_3PCl_2 in methyl cyanide and was followed conductometrically. The conductance of the Ph_3PCl_2 solution

rose uniformly with the addition of Et_4NCl but there was no suggestion of an inflection in the titration graph at 1:1 ratio as would be expected if reaction (17) had in fact occurred. Also, a 1:1 adduct ($Et_4NClPh_3PCl_2$) containing the $Ph_3PCl_3^-$ ion could not be isolated. Thus, we were not able to obtain evidence in support of ionisation (16); and the structure $Ph_3PCl^+ Cl^-$ for Ph_3PCl_2 in solution was thus assumed.

Recently ^{31}P NMR studies[27] also suggest that Ph_3PCl_2 is completely ionised in methyl cyanide solution according to the scheme (15).

The behaviour of triphenylphosphorus and arsenic dichlorides in nitrobenzene was also studied. The molar conductances of Ph_3AsCl_2 and Ph_3PCl_2 were measured at 25°; they are respectively 0.45 and 3.0 ohm^{-1} cm^2 $mole^{-1}$ at a molar concentration of .01 mole per litre. The very low Λ_m for Ph_3AsCl_2 is interpreted as indicating non-ionic behaviour of this compound in nitrobenzene. For Ph_3PCl_2 the small but significant value of molar conductance implies weak electrolytic behaviour (i.e. partial ionisation). The observed molecular weight of Ph_3PCl_2 in nitrobenzene was found to be 272.0, which suggests that ionisation

$$Ph_3PCl_2 \rightleftharpoons Ph_3PCl^+ + Cl^-$$

occurs to an extent of almost 25%.

(2) Conductometric Analysis of the System Ph_3MCl_2 - Hal_2.

The reactions of Ph_3MCl_2 (M = P, As, Sb) with halogens (I_2 and Br_2) and interhalogens (IBr, ICl and ICl_3) were studied by conductometric titration, and it was found that the graphs obtained fell into three types

depending on the particular pair of compounds involved. The three types are shown in Figure 7; they were obtained from the following systems.

Type 1	Type 2	Type 3
Ph_3PCl_2 - ICl	Ph_3PCl_2 - Br_2	Ph_3SbCl_2 - Br_2
Ph_3PCl_2 - IBr	Ph_3PCl_2 - I_2	Ph_3SbCl_2 - I_2
Ph_3PCl_2 - ICl_3	Ph_3AsCl_2 - Br_2	Ph_3SbCl_2 - ICl
Ph_3AsCl_2 - ICl	Ph_3AsCl_2 - I_2	Ph_3SbCl_2 - IBr
Ph_3AsCl_2 - IBr	-	Ph_3SbCl_2 - ICl_3
Ph_3AsCl_2 - ICl_3	-	-

Systems giving a Type 1 Graph.

The conductometric titration graphs with their definite inflections at the 1:1 ratio give a clear indication of tetrahalide formation in these systems.

e.g. $Ph_3PCl_2 + ICl \longrightarrow Ph_3PCl_3I \rightleftharpoons Ph_3PCl^+ + ICl_2^-$.

Systems giving a Type 2 Graph.

As can be seen, a type 2 graph consists of a gradual rise in conductance with a levelling off just beyond the 1:1 ratio, but with no sharp inflection at this ratio. There is however no doubt that the components are interacting to produce a tetrahalide as in the previous cases.

e.g. $Ph_3PCl_2 + Br_2 \longrightarrow Ph_3PCl_2Br_2 \rightleftharpoons Ph_3PCl^+ + Br_2Cl^-$.

This is amply confirmed by the high value of molar conductance near the 1:1 ratio and by identification of the trihalide ion from the U.V. spectrum of the solution as the reaction proceeds. The rather indefinite break in graph at 1:1 ratio is attributed to the effect of disproportionation of the trihalide ion, I_2Cl^- or Br_2Cl^- formed in these systems. These

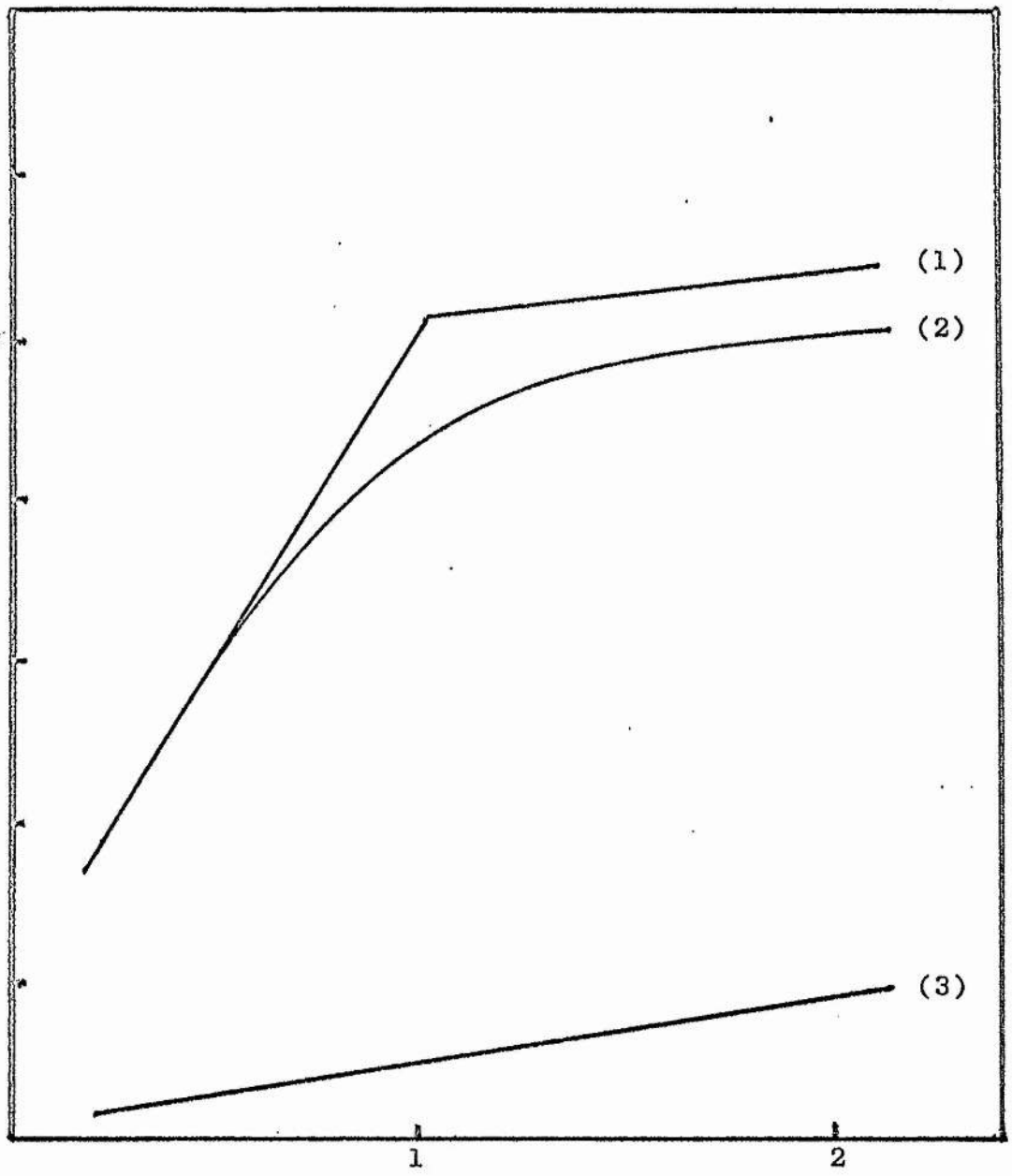


Fig. 7. Conductometric Analysis of the Systems Ph_3MCl_2 - Halogen

particular ions belong to the class of unsymmetrical trihalide ions and are known to disproportionate readily.[82]

Systems giving a Type 3 Graph.

There is no apparent interaction of the dihalide with halogen. The gradual increase in conductance can be attributed to the conductance of the added halogen itself.

The following table (Table 9) lists the tetrahalides indicated by the conductometric titration experiments, along with values of their molar conductances.

Table 9. Tetrahalides indicated by conductometric Titrations of Ph_3MCl_2 with Halogens.

Tetrahalide Indicated	Λ_m $ohm^{-1}cm^2mole^{-1}$	c_m mole/l
Ph_3PCl^+ ICl_2^-	130.0	.0029
Ph_3PCl^+ I_2Cl^-	83.2	.0027
Ph_3PCl^+ $IBrCl^-$	123.4	.0026
Ph_3PCl^+ Br_2Cl^-	86.5	.0032
Ph_3PCl^+ ICl_4^-	132.5	.0033
Ph_3AsCl^+ ICl_2^-	103.0	.0094
Ph_3AsCl^+ I_2Cl^-	78.5	.0056
Ph_3AsCl^+ $IBrCl^-$	103.5	.0063
Ph_3AsCl^+ Br_2Cl^-	80.6	.0038
Ph_3AsCl^+ ICl_4^-	119.0	.0029

The reactions of Ph_3AsBr_2 with iodine chloride and iodine trichloride were also studied. The conductometric titrations each gave a 1:1 inflection and at this ratio the U.V. spectrum of the solution showed the presence of IBr_2^- ion (λ_{max} 256 mμ). The crystalline adduct $Ph_3AsClIBr_2$ was isolated at the 1:1 mole ratio in each case, suggesting that the following reactions are taking place.

$$Ph_3AsBr_2 + ICl \longrightarrow Ph_3AsCl^+ \; IBr_2^-$$

$$Ph_3AsBr_2 + ICl_3 \longrightarrow Ph_3AsCl^+ \; IBr_2^- + Cl_2$$

These two reactions provide further confirmation for the general rule[25,26] that in the mixed tetrahalides the cation contains the halogens of lower atomic number.

Adducts isolated:

Although many of the adducts shown to be present in solution could not be isolated as pure crystalline materials, there is no reason to doubt their existence. The difficulty in isolation seems to be due firstly to the lower stability of certain of the trihalide ions in that they disproportionate in solution to halogen, halide and other trihalide ions. The second reason is the great susceptibility of M-Cl bond to traces of moisture in solvent, thus making the handling of material very difficult.

The properties of these crystalline adducts which were obtained analytically pure are summarised in Table (10).

Table 10. Crystalline Adducts of Ph_3M with Halogens.

Compounds	Colour	m.p. °C	Λ_m at 25° $ohm^{-1}\ cm^2\ mole^{-1}$	c_m mole/l
Ph_3PICl_3	Yellow	94-95	114.0	.01
Ph_3AsICl_3	Yellow	80-81	108.0	.01
Ph_3AsICl_5	Yellow	122-124	117.5	.01
Ph_3AsIBr_2Cl	Red	92-94	107.4	.01

(3) Reactions of Ph_3MCl_2 with Halogens in moist methyl cyanide.

The foregoing section clearly shows that Ph_3AsCl_2 reacts readily with halogens and interhalogens to give crystalline tetrahalides containing the chlorotriphenylarsonium cation Ph_3AsCl^+. This is in conflict with results reported by Beveridge who carried out some preliminary experiments on reactions of Ph_3AsCl_2 and halogens.[71] On the basis of analytical results alone, Beveridge concluded that the materials isolated from solution were tetraphenylarsonium trihalides and that the reactions must have followed a course in which phenyl migration had occurred.

$$\text{e.g.}\quad 2\ Ph_3AsCl_2 + ICl \longrightarrow Ph_4As^+\ ICl_2^- + Ph_2AsCl_3$$

In some experiments in the present work involving these particular reactants carried under conditions in which the usual stringent precautions

against the intrusion of moisture were not observed, yellow crystals (m.p. 83-84°) were obtained and these analysed well for $Ph_4As^+ ICl_2^-$. The infrared spectrum of the compound, however, showed strong broad absorption at 3000 - 2290 cm^{-1} and two peaks at 760 and 780 cm^{-1}. None of these peaks was observed in a genuine sample of $Ph_4As^+ICl_2^-$, synthesised for comparison. The absorption at 3000-2290 cm^{-1} had the appearance of the characteristic absorption for the Ph_3AsOH^+ ion[83], and the peaks at 760 and 780 cm^{-1} have been assigned to the As-O stretching frequencies.[50] These data can be explained by the formulation of a mixed anion compound $(Ph_3AsOH^+)_2ICl_2^-Cl^-$. Analytical results (% found and calculated) are listed in Table (11).

Table 11. Analytical Data for $(Ph_3AsOH^+)_2ICl_2^-Cl^-$

Analysis	%C	%H	%As	%Cl	%I	m.p. °C.
Found (present work)	49.26	3.44	17.22	12.24	14.40	83-84
Found (Beveridge[71])	49.70	3.70	-	12.10	-	84-85
$(Ph_3AsOH^+)ICl_2^-Cl^-$	49.12	3.64	17.10	12.12	14.44	-
$Ph_4As^+ ICl_2^-$	49.60	3.45	12.90	12.20	21.80	192

Examples of compounds containing two different anions are not unknown[84], and in fact a closely similar compound $(Ph_3AsOH^+)_2Br_3^- Br^-$ has been reported recently[83].

The ultraviolet spectrum of the compound shows the presence of ICl_2^- (λ_{max} 236 mμ) ion and the extinction coefficient (ε, 311) calculated on the basis of the above formula was in good agreement with the published value.[79]. In solution the compound $(Ph_3AsOH^+)_2ICl_2^-\ Cl^-$ would be expected to behave as an equimolar mixture of $Ph_3AsOH^+\ ICl_2^-$ and $Ph_3As(OH)Cl$; since this latter compound is a weak electrolyte in methyl cyanide, the following equilibria would result

$$(Ph_3AsOH^+)_2\ ICl_2^-\ Cl^- \rightleftharpoons Ph_3AsOH^+ + ICl_2^- + \underbrace{Ph_3AsOH^+ + Cl^-}$$

$$\downarrow\uparrow$$

$$Ph_3As(OH)Cl.$$

In support of these equilibria the value of the molar conductance of $(Ph_3AsOH^+)_2ICl_2^-\ Cl^-$ in methyl cyanide is that expected for a strong 1:1 electrolyte (Λ_m = 143.50; c_m = .0024 mole/l); in addition, the compound could also be isolated from methyl cyanide containing equimolar quantities of $Ph_3As(OH)Cl$ and $Ph_3As(OH)^+\ ICl_2^-$. The conductometric titration of the compound with iodine chloride gave a break at 1:1 mole ratio indicating that the reaction;

$$(Ph_3AsOH^+)_2\ ICl_2^-\ Cl^- + ICl \longrightarrow 2\ Ph_3AsOH^+\ ICl_2^-$$

is taking place.

Similarly, from their infrared spectra the products from the reactions Ph_3AsCl_2/I_2 and Ph_3AsCl_2/IBr in moist solvents were found to contain Ph_3AsOH^+: these products were not investigated fully.

There would seem to be no doubt that the compounds Beveridge obtained were the same ones as those obtained in the present work, and that interpretation of these as tetraphenylarsonium trihalides is erroneous.

Since in these reactions Ph_3AsCl_2 is involved and since the As-Cl bond is much more susceptible to hydrolysis than the As-Br or As-I bond, the formation of hydroxy-arsonium compounds is understandable.

SUMMARY

The systems Ph_3M-Hal_2 (M = P, As or Sb; Hal_2 = ICl or ICl_3) and Ph_3MCl_2-Hal_2 (Hal_2 = Br_2, I_2, ICl, IBr, ICl_3) have been studied by the method of conductometric titration which has demonstrated the existence in methyl cyanide of the triphenylphosphorus and -arsenic tetrahalides, $Ph_3MCl_nI_{4-n}$ and $Ph_3MCl_nBr_{4-n}$. For triphenylstibine, the formation of only one tetrahalide, Ph_3SbClI_3, was indicated. The chlorine containing tetrahalides of phosphorus and arsenic behave as strong 1:1 electrolytes in methyl cyanide and their modes of ionisation parallel that of the analogous compounds of general formula $Ph_3MBr_nI_{4-n}$; that is, ionisation occurs to give the cation containing the halogen atom of lower atomic number.

e.g. $Ph_3PI_2Cl_2 \longrightarrow Ph_3PCl^+ I_2Cl^-$

$Ph_3AsBr_2Cl_2 \longrightarrow Ph_3AsCl^+ Br_2Cl^-$

Conductance measurements have been made on methyl cyanide and nitrobenzene solutions of the dichlorides Ph_3MCl_2 (M = P, As, Sb), and by comparison of molar conductance values for .01 M solutions it has been concluded that the tendency towards covalency increases with increasing atomic number of the element M. The results obtained from the conductometric titrations of Ph_3MCl_2/Hal_2 were in keeping with the behaviour of Ph_3MCl_2 in solution. Ph_3PCl_2 and Ph_3AsCl_2, which are strong and weak electrolytes respectively in methyl cyanide, readily add another mole of halogen to produce the tetrahalides of the type $Ph_3MCl^+(ClHal_2)^-$ or Ph_3MCl^+ $(ClHal'\ Hal'')^-$. Ph_3SbCl_2, which is effectively non-ionic, does not react with halogens to form tetrahalides.

Many of the adducts indicated by the conductometric titrations were isolated as crystalline solids; whereas others could not be obtained pure. This latter fact is attributed to two things: firstly, to the ready dissociation of the unsymmetrical trihalide ions I_2Cl^-, Br_2Cl^-, and secondly to the great moisture sensitivity of M-Cl bonds compared to M-Br bonds. The properties of the crystalline adducts isolated are summarised in Table 12. None of these has been reported before.

Table (12). Crystalline Adducts of Ph_3M with Halogens.

Adducts	Colour	m.p. °C	Λ_m ohm.$^{-1}$cm.^{2}mole.$^{-1}$ at 25°	c mole/l.
Ph_3PICl	Yellow	122-125	67.6	.01
Ph_3PICl_3	Yellow	94- 95	114.0	.01
$[(Ph_3P)_2Cl]I_3$	Yellow	218	127.2	.01
$[(Ph_3P)_2Br]HgBr_3$	White	130	117.5	.01
Ph_3AsICl_3	Yellow	80- 81	108.0	.01
Ph_3AsIBr_2Cl	Red	92- 94	107.4	.01
Ph_3AsICl_5	Yellow	122-124	117.5	.01
$(Ph_3AsOH)_2ICl_3$	Yellow	83- 84	143.5	.0024
Ph_3SbICl*	White	159-161	2.4†	.01
$(Ph_3SbI)_2O$	Red	195-198	-	-

*previously reported as an impure product.[85]

†not a true value because of slow molecular dissociation.

PART II

HALOGEN ADDUCTS OF PERFLUOROPHENYL -PHOSPHINES AND -ARSINES

I N D E X

INTRODUCTION

Since their discovery in 1952, the fluoroalkyl derivatives of group V elements have been extensively studied by many workers.[86,87] The corresponding fluoroaryl derivatives on the other hand have received much less attention and it is only relatively recently that interest in the chemistry of these compounds is becoming more apparent.

Initial lack of interest in these compounds can be attributed in part to the absence of suitable synthetic methods, and of special significance in this connection was the synthesis, by Tatlow and co-workers, of the Grignard reagent, pentafluorophenylmagnesium bromide.[88] This compound has proved to be very useful as a starting material for a wide range of pentafluorophenyl derivatives.

In 1960, Wall et.al. reported the preparation of tris(pentafluorophenyl)phosphine by the reaction of phosphorus (111) chloride with pentafluorophenylmagnesium bromide.[66] Immediately thereafter, Glemser et.al. reported the preparation of the derivatives $(C_6F_5)_3M$ (M = P, As and Sb) by a similar Grignard reaction, and claimed that the antimony derivative is more susceptible to hydrolysis than the phosphorus and arsenic compounds.[68]

The substituted derivatives $(C_6F_5)_nM\ Hal_{3-n}$ (M = P, As. Hal = Cl or Br) have been obtained by the reaction of pentafluorophenylmagnesium bromide and the corresponding M (III) halide in the appropriate mole ratios.[89,90]

The replacement of hydrogen by fluorine in triphenylphosphine has been shown to result in a stronger interaction between the unshared electron pair of the phosphorus atom and the pi-electron system of the aromatic nucleus. Thus tris(pentafluorophenyl)phosphine is more acidic in the Lewis sense than triphenylphosphine and does not react in the usual way with acids or with alkyl halides;[66] also, it does not form a complex with BF_3,[91] and it is converted to tris(pentafluorophenyl)-phosphine oxide only through strong oxidation.[66]

The substituted phosphorus (111) chlorides, $(C_6F_5)_nPCl_{3-n}$, have been shown to react with chlorine to produce chlorophosphoranes.

$$(C_6F_5)_n\ PCl_{3-n} + Cl_2 \longrightarrow (C_6F_5)_n\ PCl_{5-n}$$

$(C_6F_5)_2PCl_3$ and $(C_6F_5)_3PCl_2$ have been isolated as crystalline solids and $C_6F_5PCl_4$ as an unstable yellow solid.[92-94]

The fluorophosphoranes $(C_6F_5)_nPF_{5-n}$ have been prepared by the reaction of the analogous chlorophosphoranes with antimony or arsenic trifluorides.[95]

$$(C_6F_5)_n\ PCl_{5-n} \xrightarrow{SbF_3 \text{ or } AsF_3} (C_6F_5)_n\ PF_{5-n}$$

There is no mention in the literature of the corresponding bromo- and iodophosphoranes prior to the recent publication by Harris and Ali.[96]

In contrast with the pentafluorophenyl compounds of phosphorus, little has been reported on the chemistry of the corresponding arsenic derivatives, and there is no mention in the literature of the pentafluorophenyl substituted arsenic (V) halides, $(C_6F_5)_n\ As\ Hal_{5-n}$.

To date, the only reported halide of type $(C_6F_5)_nSbHal_{3-n}$ is chlorobis(pentafluorophenyl)antimony,[97] and antimony (V) compounds of type $(C_6F_5)_nSbHal_{5-n}$ are not known.

Considerable interest attaches to the halogenopentafluorophenyl derivatives $(C_6F_5)_nM\ Hal_{5-n}$, since they are in effect pentahalides of the element M in which one or more of the halogen atoms has been replaced by the fairly strongly electronegative C_6F_5 group. Estimates put the electronegativity value of this group at approximately 2.60 (on the Pauling Scale)[98]; thus the electronegativity of the pentafluorophenyl group lies between that of bromine (2.95) and iodine (2.56). In its compounds, therefore, it might be expected that the C_6F_5 group would display the characteristics of a heavy halogen atom.

It was, therefore, thought of considerable value to study compounds such as $(C_6F_5)_3M\ Hal_2$ to investigate whether or not the C_6F_5 group behaved as a pseudohalogen atom in these compounds and whether the electron withdrawing characteristics of the group caused the properties of these compounds to follow the general pattern observed in other compounds of the type $R_nM\ Hal_{5-n}$.

RESULTS AND DISCUSSIONS

A. Tris(pentafluorophenyl)phosphine-Halogen Systems.

(1) Tris(pentafluorophenyl)phosphorus Dichloride.

(a) Preparation and Stability:-

Tris(pentafluorophenyl)phosphorus dichloride was first prepared by Emeléus and Miller, from the direct reaction ~~under vacuum~~ of chlorine and tris(pentafluorophenyl)phosphine or tris(pentafluorophenyl)phosphine sulphide.[93]

$$(C_6F_5)_3P + Cl_2 \longrightarrow (C_6F_5)_3PCl_2$$

$$(C_6F_5)_3PS + 2Cl_2 \longrightarrow (C_6F_5)_3PCl_2 + SCl_2.$$

We have found that a simpler method giving a good yield (ca. 80%) of pure product is to pass chlorine into a methyl cyanide solution of $(C_6F_5)_3P$.[96] In this way tris(pentafluorophenyl)phosphorus dichloride precipitates as a white, crystalline, moisture sensitive, solid (m.p. 229-232°). Because of ready hydrolysis of the compound to $(C_6F_5)_3PO$ in atmospheric moisture it must be handled under strictly anhydrous conditions. Precautions were therefore taken to ensure the absence of moisture at all stages in its study.

(b) Electrolytic Conductance of $(C_6F_5)_3PCl_2$ in methyl cyanide:-

$(C_6F_5)_3PCl_2$ is moderately soluble in methyl cyanide and the resultant solution is quite stable. For this reason and on account of its high dielectric constant (36.7 at 25°) methyl cyanide was chosen as a solvent for this and the following conductance studies, conductances were measured over a range of concentration at 25°. After an initial

rise due to warming up of the solutions from room temperature to 25°, the specific conductance of the solutions remained steady. Molar conductances (Λ_m) were calculated from the steady values of the specific conductance (K), and the results are shown in Table (13).

Table 13. Conductance of Tris(pentafluorophenyl)-phosphorus dichloride in Methyl cyanide at 25°C

c_m mole/l.	$10^4 K$ ohm.$^{-1}$cm.$^{-1}$	Λ_m ohm.$^{-1}$cm.^{2} mole.$^{-1}$
0.0029	0.027	0.94
0.0061	0.042	0.69
0.0086	0.046	0.54
0.0110	0.052	0.47
0.0140	0.061	0.44
0.0190	0.061	0.32

The plot of Λ_m against $\sqrt{c_m}$ is a straight line and Λ_m at 0.01 mole/litre is 0.5 ohm.$^{-1}$cm.^{2}mole.$^{-1}$. From a comparison of the values of molar conductance at c_m = .01 mole/litre for the following compounds,

Compound	Λ_m ohm.$^{-1}$cm.^{2}mole.$^{-1}$
Ph_3PCl_2.....	78 [26]
$(PhO)_3PCl_2$.....	105 [56]
PCl_5.....	135 [10]
$(C_6F_5)_3PCl_2$.....	0.5

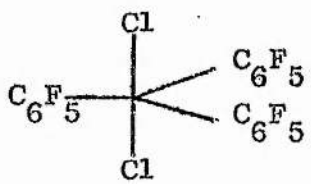
it is seen that in relation to other PR_nHal_{5-n} compounds, $(C_6F_5)_3PCl_2$ is virtually a non-electrolyte in methyl cyanide.

(c) Conductometric Titration Study of the $(C_6F_5)_3P/Cl_2$ System.

A conductometric analysis of the system $(C_6F_5)_3P/Cl_2$ was carried out in methyl cyanide solution in a vacuum system specially designed for titrations using chlorine (see experimental section, p.112 Fig. 16). In this way small amounts of chlorine of known weight (0.052 m.mole lots) were distilled into a cell containing a solution of tris(pentafluorophenyl)phosphine in methyl cyanide; the conductance was measured after each addition. The conductance value of the phosphine solution rose only very slightly from its near zero value and the solution remained colourless, until the 1:1 (Cl_2: $(C_6F_5)_3P$) mole ratio was reached. There was no significant change in conductance beyond the 1:1 ratio and the solution assumed a greenish yellow colour (i.e. the colour of a chlorine solution). Thus, the formation of the colourless, non-electrolyte, $(C_6F_5)_3PCl_2$, (Λ_m = 0.42 ohm.$^{-1}$ cm.^{2} mole.$^{-1}$; c_m = 0.022 mole/l.) by the reaction $(C_6F_5)_3P + Cl_2 \longrightarrow (C_6F_5)_3PCl_2$ was confirmed.

It is interesting to compare our findings with the recently published work of Emeléus and Miller.[93] These authors have shown the presence of penta-covalent phosphorus in the compound $(C_6F_5)_3PCl_2$, from the mass spectrum and ^{31}P - NMR studies.

The pentafluorophenyl group has been shown to be less electronegative than the chlorine atom, and being the less electronegative ligand it would be expected to occupy equatorial sites if the molecular geometry is assumed to be trigonal bipyramidal (structure A) as is found in Me_nPF_{5-n}.[99]



[A]

In keeping with the proposed symmetrical structure (A), the infra-red spectrum of $(C_6F_5)_3PCl_2$ shows only a single, very low frequency P-Cl absorption (νPCl_2, 362 cm.$^{-1}$).

The difference in behaviour between $(C_6H_5)_3PCl_2$ and $(C_6F_5)_3PCl_2$ may be accounted for in terms of the much higher electronegativity of the C_6F_5 group as compared with the C_6H_5 group. The inductive effect of the fluorine atoms in $(C_6F_5)_3P$ will decrease the electron density on the phosphorus atom so that this is more electronegative when attached to C_6F_5 groups than when attached to C_6H_5 groups. From a simple electrostatic argument it would therefore seem less likely for a chlorine atom to break away as Cl^- in the pentafluorophenyl compound. Also it is clear that

the strength of the P-Cl bond will be affected by the electronegativity of the phosphorus atom. It has in fact been shown recently from a study of R_3PF_2 compounds (R = Me, Et, Bu, Pr, F) that the P-F bond distances become smaller as the electronegativity of the group R increases (Me to F); as the electronegativity of the attached group increases the effective nuclear charge on the phosphorus atom increases and so the P-F separation may reasonably be expected to decrease.[100]

(2) The Reaction of Tris(pentafluorophenyl)phosphine and Bromine.

(a) Conductometric Titration:-

A conductometric titration study of the $(C_6F_5)_3P$-Br_2 system in methyl cyanide gave the results recorded in Table (14), and graph illustrated in Figure (8)

Table (14) Conductometric Analysis of the System Tris(pentafluorophenyl)phosphine-Bromine.

Mole ratio $(Br_2:(C_6F_5)_3P)$	$K \times 10^4$ ohm.$^{-1}$ cm.$^{-1}$	Mole ratio $(Br_2:(C_6F_5)_3P)$	$K \times 10^4$ ohm.$^{-1}$ cm.$^{-1}$
0.00	.004	1.57	9.35
0.19	1.31	1.77	11.29
0.38	2.05	1.96	12.85
0.58	2.62	2.17	13.45
0.78	3.12	2.34	14.25
0.98	3.59	2.57	14.65
1.19	5.90	2.74	15.00
1.36	7.69	2.94	15.30
1.46	8.49	-	-

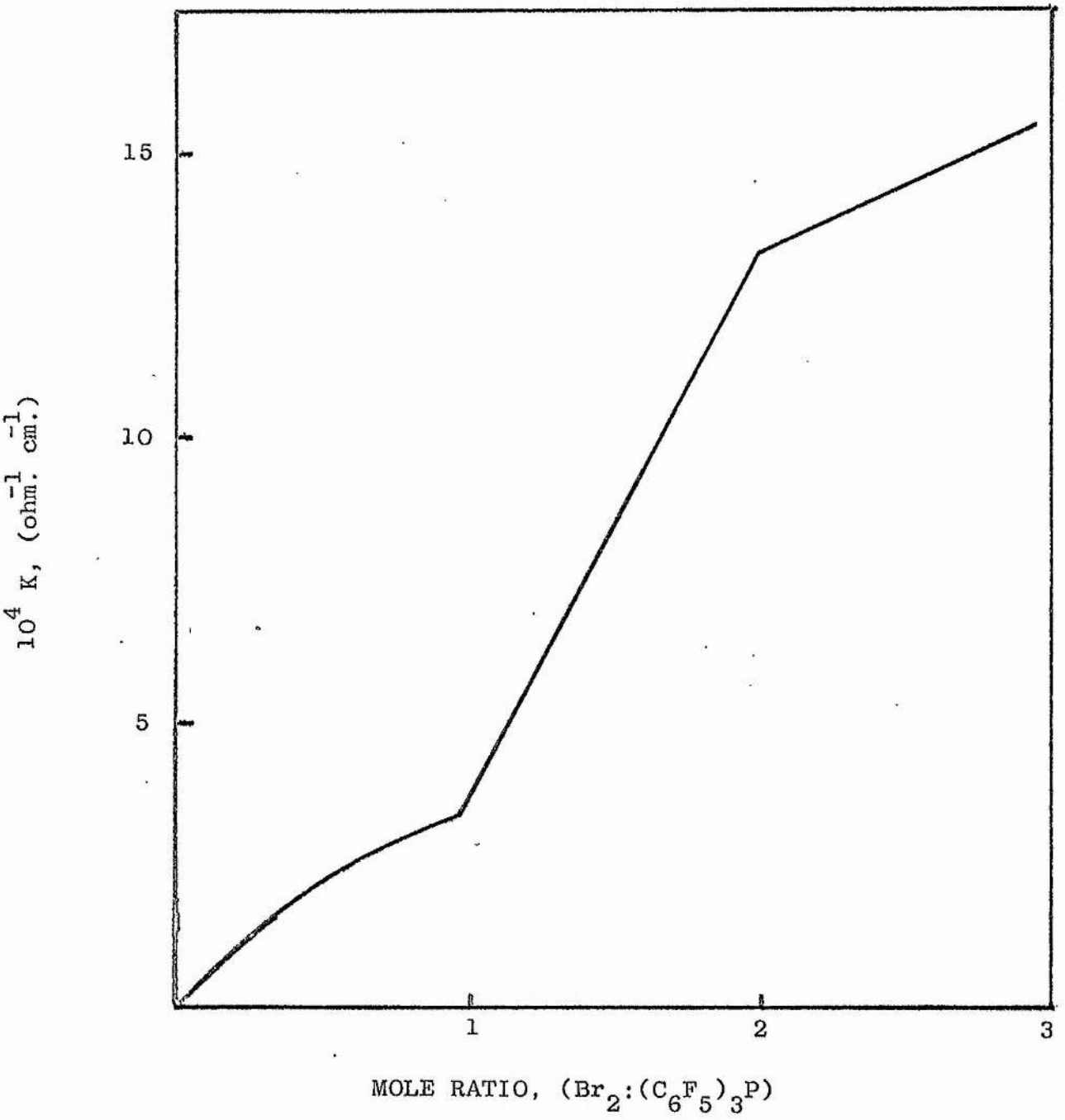


Fig. 8. Conductometric Analysis of the System Tris(pentafluorophenyl)phosphine-Bromine

It is of interest that the configuration of this titration graph resembles that of the system Ph_3As-Br_2, in which case both the 1:1 and 2:1 products, i.e. Ph_3AsBr_2 and Ph_3AsBr_4 were isolated.[25]

The conductance graph (Fig. 8) shows a gently rising slope up to the 1:1 (Br_2: $(C_6F_5)_3P$) mole ratio when the solution was colourless, and after the 1:1 ratio the solution became yellow and the conductance rose sharply until the 2:1 ratio, at which point there was another marked change in gradient. The inflections at 1:1 and 2:1 mole ratios clearly indicate the formation in solution of the compounds $(C_6F_5)_3PBr_2$ and $(C_6F_5)_3PBr_4$. The molar conductance value at the 1:1 (Λ_m = 26.2 ohm.$^{-1}$ cm.^{2} mole.$^{-1}$; c_m = 0.15 mole/1.) and 2:1 ratio (Λ_m = 106.1 ohm.$^{-1}$ cm^2.mole.$^{-1}$; c_m = .012 mole/1.) show that these compounds are weak and strong electrolytes respectively. Ultraviolet examination of the solution indicated the formation of tribromide ion beyond the 1:1 ratio. The reactions taking place in solution may be represented thus:

$$(C_6F_5)_3P + Br_2 \longrightarrow (C_6F_5)_3PBr_2 \xrightarrow{+\,Br_2} (C_6F_5)_3PBr_4$$

$$(C_6F_5)_3PBr_2 \rightleftharpoons (C_6F_5)_3PBr^+Br^- \qquad (C_6F_5)_3PBr_4 \rightleftharpoons (C_6F_5)_3PBr^+\,Br_3^-$$

Attempts were made to prepare the 1:1 adduct, $(C_6F_5)_3PBr_2$, both by ether precipitation from methyl cyanide solution, and by the direct reaction of bromine and the phosphine. Ether addition to methyl cyanide containing equimolar quantities of $(C_6F_5)_3P$ and bromine yielded no precipitate, and on the evaporation of solvent from this solution,

$(C_6F_5)_3P$ was recovered. Direct mixing of bromine and $(C_6F_5)_3P$ (1:1 ratio) in a sealed tube under vacuum resulted in the formation of a yellow product, which after washing with anhydrous ether was identified as $(C_6F_5)_3PBr_4$. Tris(pentafluorophenyl)phosphorus tetrabromide was also obtained as an unstable (bromine evolved) yellow solid by ether precipitation of a methyl cyanide solution containing bromine and tris(pentafluorophenyl) phosphine in the 2:1 mole ratio.

(b) Vapour Pressure Study:-

In view of the ready decomposition of the tris(pentafluorophenyl) phosphine-bromine adducts it was thought that a vapour pressure study of the system may provide valuable information about the stoicheiometry of the solid phases in this system.

The interaction of bromine and tris(pentafluorophenyl)phosphine was studied by measurement of the vapour pressures of different compositions of the mixture at 0° (spiral gauge method; for experimental details see P. 109 , Fig. 15). The phase diagram is reproduced in Figure (9). This shows the formation of only two solid adducts stable at 0° within the range of composition studied. These are the above mentioned tetrabromide, $(C_6F_5)_3PBr_4$, and a decabromide, $(C_6F_5)_3PBr_{10}$. This latter compound, by analogy with $Me_4N^+Br_9^-$, may be written as $(C_6F_5)_3PBr^+ Br_9^-$. [101]

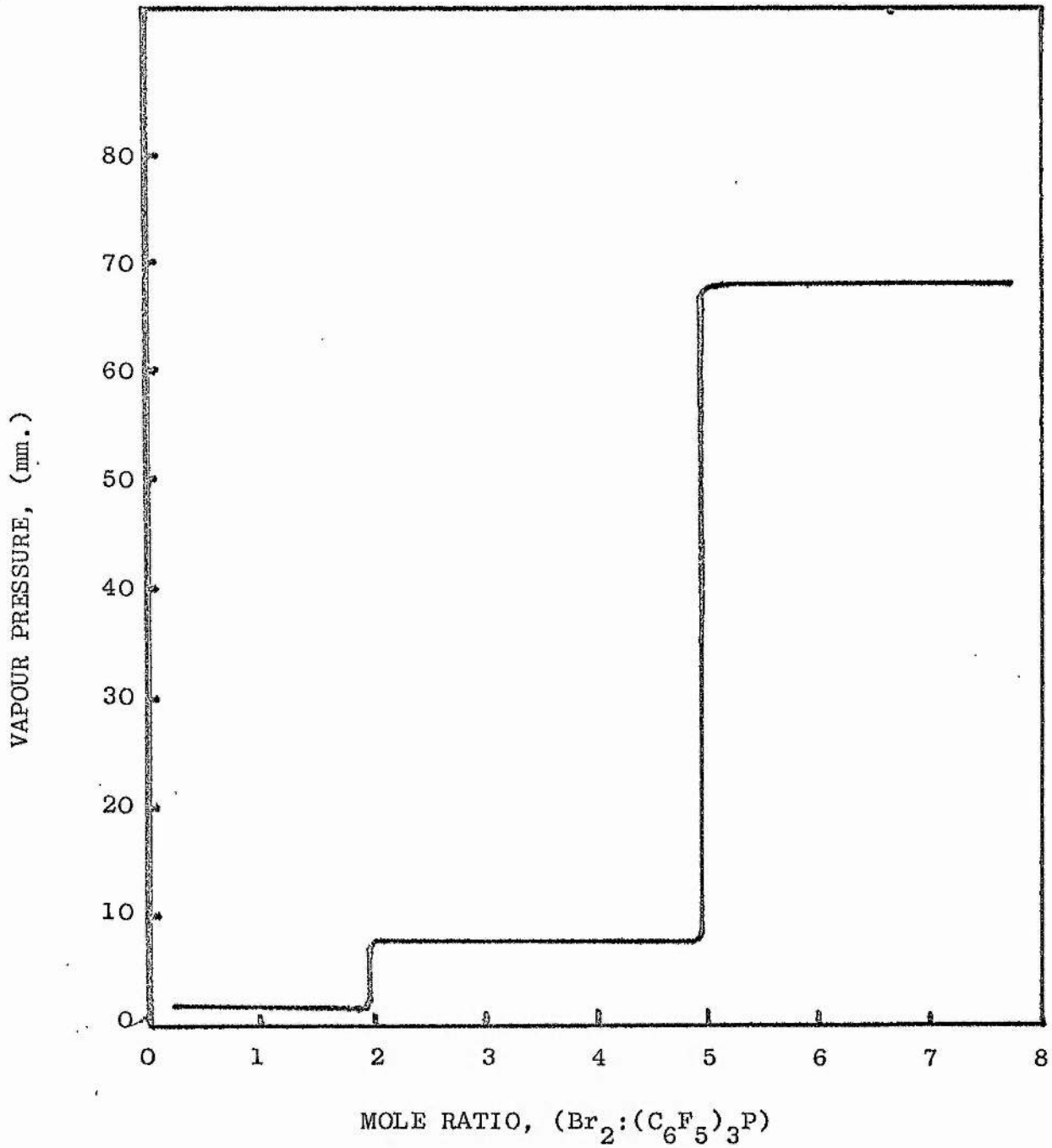


Fig. 9. The Vapour pressures of mixtures of $(C_6F_5)_3P$ and Br_2 at 0^oC

The phase diagram shows quite clearly that the compound $(C_6F_5)_3PBr_2$ is not a stable entity in the solid state. This is in contrast to the results of the conductometric titration studies which showed that it exists under suitable conditions in solution.

It is interesting that the dihalides, $(C_6F_5)_3PCl_2$ and $(C_6F_5)_3PBr_2$, should possess such different conducting properties in methyl cyanide solution (Λ_m values, $(C_6F_5)_3PCl_2$ = 0.5 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .01 mole/l.; $(C_6F_5)_3PBr_2$ = 26.2 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .015 mole/l.). To explain why the former compound is a non-conductor and the latter a conductor it is necessary to consider the strength of P-Hal bonds and the size of the halogen atoms. In the trihalides of phosphorus the P-Hal bonds-strength diminish in the order P-F > P-Cl > P-Br > P-I, and it is unlikely that this order would be reversed in the $R_3P\ Hal_2$-type compounds. Thus, heterolytic fission of the P-Hal bond to produce Hal^- ion should be easier for P-Br than P-Cl. This trend is also observed in Me_nPHal_{5-n} compounds. When Hal = F the compounds are exclusively molecular whereas when Hal = Cl an ionic structure is adopted.[43,53]

Steric hindrance, in the present case involving the large bromine atom and pentafluorophenyl group, may also contribute to the greater ease with which the bromine atom comes away as a Br^- ion.

(c) <u>The Reaction of $(C_6F_5)_3PBr_2$ with some halogens in methyl cyanide solution.</u>

To obtain further evidence for the formation of the weak electrolyte, $(C_6F_5)_3PBr_2$ in the $(C_6F_5)_3P/Br_2$ reaction in methyl cyanide, conductometric titrations of $(C_6F_5)_3PBr_2$ with iodine and iodine bromide were carried out. The $(C_6F_5)_3PBr_2$ was prepared in situ by mixing equimolar quantities of bromine and tris(pentafluorophenyl)phosphine in the solvent.

The conductance-composition graphs of both titrations were remarkably similar and showed a rise in conductance followed by a break close to the 1:1 mole ratio. The high molar conductance values of the solution at the 1:1 mole ratio

(IBr - titration, Λ_m = 121.0 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .026mole/l.

I_2 - titration, Λ_m = 113.1 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .0086 mole/l.)

supports the formulation of the adducts as strong 1:1 electrolytes and examination of the ultraviolet spectra of the solutions confirmed the presence of trihalide ion (IBr_2^-, $\lambda_{max.}$ = 257mμ; I_2Br^-, $\lambda_{max.}$ = 278 mμ). By analogy with the Ph_3AsBr_2/Hal_2 system[25], the reactions occurring are thus:-

$$(C_6F_5)_3PBr_2 + IBr \longrightarrow (C_6F_5)_3PBr^+ + IBr_2^- \quad \ldots\ldots\ldots(18)$$

$$(C_6F_5)_3PBr_2 + I_2 \longrightarrow (C_6F_5)_3PBr^+ + I_2Br^- \quad \ldots\ldots\ldots(19)$$

These conductometric titrations therefore support the existence of $(C_6F_5)_3PBr_2$ in solution. Attempts to isolate the compounds indicated by reactions (18) and (19) produced reddish oils which could not be crystallised; however, the halogen analysis of these oils was very close to the required values.

(3) The Reaction of Tris(pentafluorophenyl)phosphine and Iodine.

A conductometric analysis of the system $(C_6F_5)_3P$-I_2 was carried out in methyl cyanide solution and the conductance graph is reproduced in Figure (10).

(a) Reaction at room temperature:-

Unlike triphenylphosphine which readily reacts with iodine, tris(pentafluorophenyl)phosphine was found to react very slowly. A distinct variation of specific conductance with time was observed at each stage during the titration. The conductance of the solution rose, at first rapidly and then more slowly, to a steady value after about an hour. Sufficient time was allowed after each addition of the iodine solution to the phosphine solution to obtain steady conductance values. The originally colourless phosphine solution became red after the first addition of iodine and the conductance of the solution rose uniformly up to about the 2:1 (I_2: $(C_6F_5)_3P$) mole ratio when the increment in conductance after each addition of titrant began to diminish. The result was a graph (Fig. 10, (i) with a rather indefinite break near the 2:1 ratio but with no break at the 1:1 ratio. The molar conductance of the solution at the 2:1 ratio was:-

$$\Lambda_m = 51.40 \text{ ohm.}^{-1}\text{cm.}^{2}\text{mole.}^{-1} \quad (c_m = 0.01 \text{ mole./l.}).$$

The ultraviolet spectrum of the solution from just after the zero mole ratio, showed the presence of tri-iodide ion, and this suggests that the tetraiodide, $(C_6F_5)_3PI^+ I_3^-$, forms right from the beginning.

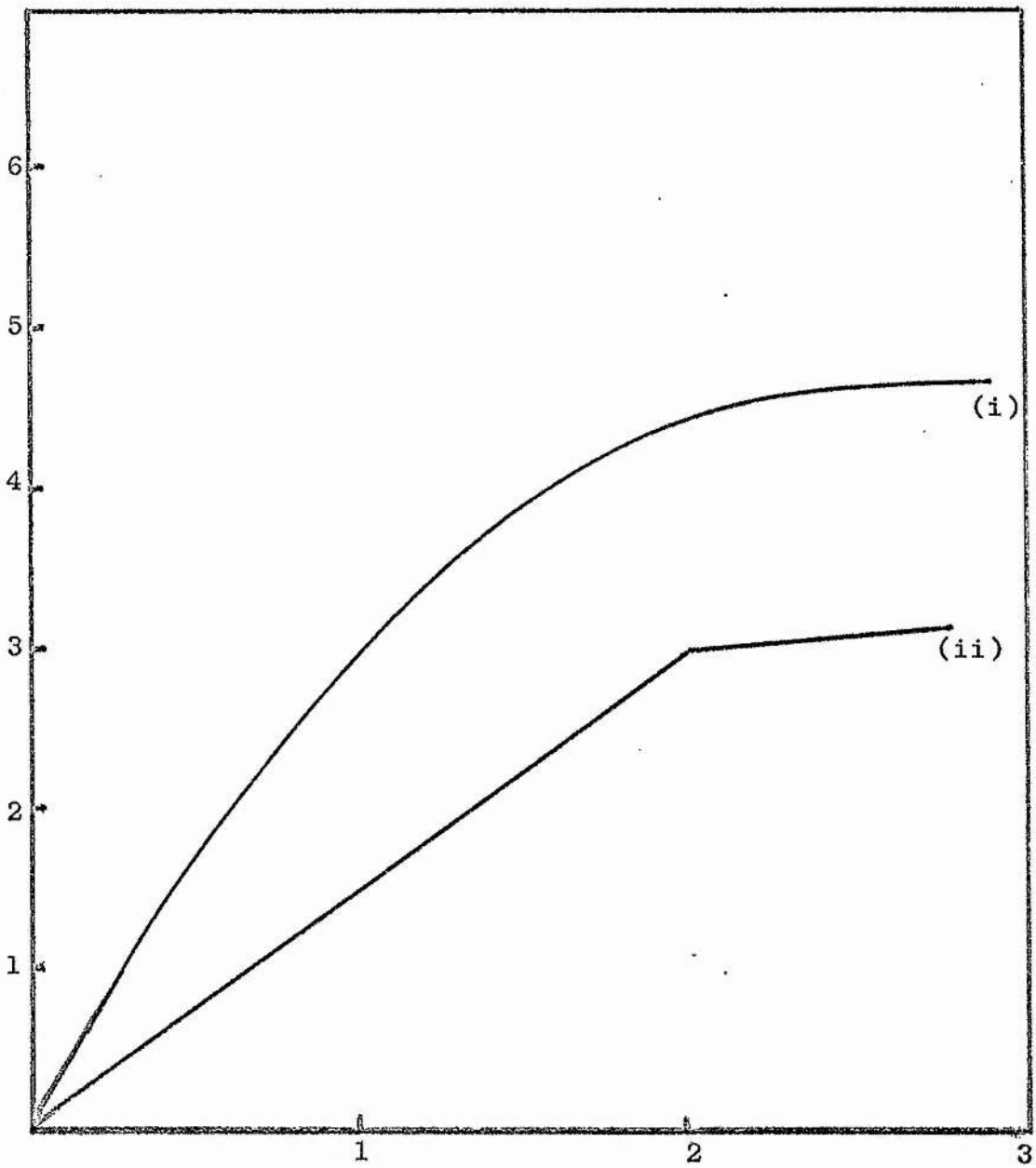


Fig. 10. Conductometric Analysis of the System Tris(pentafluorophenyl)phosphine-Iodine (i) at 18°C, (ii) at -35°C

However, the absence of a sharp break in the conductance-composition graph coupled with the low (for a strong 1:1 electrolyte in methyl cyanide) value of molar conductance at the 2:1 ratio suggests that molecular dissociation as well as ionisation of the 2:1 adduct is occurring

$$(C_6F_5)_3PI_4 \rightleftharpoons \begin{cases} (C_6F_5)_3PI^+ + I_3^- \\ (C_6F_5)_3P + 2I_2. \end{cases}$$

Support for this comes from the U.V. spectrum of the solution which has a fairly strong band at 462 mμ, attributed to molecular iodine.

(b) Reaction at -35°:-

In view of the low stability of $(C_6F_5)_3PI_4$ it was thought worthwhile to repeat the reaction at -35° at which temperature the molecular dissociation should be less. The conductometric titration was carried out in an apparatus designed for immersion in a thermostat bath. The conductance graph (Fig. 10, ii) is similar in shape to that of Ph_3As-I_2 system, and shows a definite break at the 2:1 ratio, indicating the formation of a tetrahalide, $(C_6F_5)_3PI^+ I_3^-$.

An attempt was made to isolate the compound, $(C_6F_5)_3PI_4$, by ether precipitation of methyl cyanide solution containing iodine and $(C_6F_5)_3P$ in the 2:1 ratio. The red solid which crystallised after standing at 0° decomposed rapidly into a red oil at room temperature. The halogen analysis of the oil gave slightly high value for iodine (Found: I, 52.7. calculated for $C_{18}F_{15}PI_4$: I, 48.9%).

It would seem, therefore, from the above observations, that the only product of the reaction of $(C_6F_5)_3P$ and I_2 is the tetrahalide, $(C_6F_5)_3PI_4$, which is stable only at temperatures below about 0^o. It is perhaps not surprising that $(C_6F_5)_3PI_2$ does not exist since there is a good deal of evidence pointing to the general lack of interaction between iodine and phosphorus (111) halides to produce a phosphorus (V) halide containing iodine.[102] This can be put down to the steric effect of the larger iodine atoms. In addition the low electronegativity of iodine operates against its presence in compounds containing a phosphorus atom in its higher oxidation state.

(4) The Reaction of Tris(pentafluorophenyl)phosphine and Iodine Bromide.

It was shown above that $(C_6F_5)_3PBr_2$ in methyl cyanide underwent reaction with iodine forming the tetrahalide $(C_6F_5)_3PBr_2I_2$, but that attempts to isolate the crystalline compound were not successful. An alternative approach to this compound is the reaction of $(C_6F_5)_3P$ and iodine bromide.

$$(C_6F_5)_3P + 2IBr \longrightarrow (C_6F_5)_3PBr_2I_2$$

To study this reaction $(C_6F_5)_3P$ was titrated conductometrically with iodine bromide in methyl cyanide. The originally colourless solution showed the characteristic dark colour of trihalide ion from the first addition of iodine bromide, and the conductance rose uniformly up to the mole ratio IBr: $(C_6F_5)_3P$ = 2:1, at which point there was a definite break in the graph. Thus, it would appear that $(C_6F_5)_3PIBr$ does not

exist as a stable entity in methyl cyanide, and that the reaction produces, straightaway, the highly conducting 2:1 adduct, $(C_6F_5)_3PI_2Br_2$ (Λ_m = 142.5 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .0054 mole./l.). The reaction occurring is therefore, by analogy with Ph_3As/IBr system;

$$(C_6F_5)_3P + 2IBr \longrightarrow (C_6F_5)_3PI_2Br_2 \longrightarrow (C_6F_5)_3PBr^+ + I_2Br^-.$$

The U.V. examination of methyl cyanide solutions at different IBr: $(C_6F_5)_3P$ ratios showed that the di-iodobromide ion was formed immediately in the titration ($\lambda_{max.}$, 278, 351 mμ) and up to the conductance break at the 2:1 ratio. Thereafter, the absorption peaks at 278 and 351 mμ (I_2Br^-) were replaced by a single one at 257 mμ (IBr_2^-) indicating that the process

$$Br\ I_2^- + IBr \longrightarrow IBr_2^- + I_2$$

had occurred.

Attempts were made to isolate $(C_6F_5)_3PBr_2I_2$ and $(C_6F_5)_3PBr_3I$ by mixing methyl cyanide solutions of IBr and $(C_6F_5)_3P$ in the 2:1 and 3:1 mole ratios respectively. There was no crystallisation of a solid on the addition of ether, even on cooling to -5°. On freeze drying dark oils were produced, whose analysis gave figures which corresponded with those required for these compounds. The molar conductances of these adducts determined at 25° were:

$(C_6F_5)_3PBr^+\ I_2Br^-$ = 106.0 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .01 mole/l.

$(C_6F_5)_3PBr^+\ IBr_2^-$ = 101.6 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .01 mole/l.

5. Chlorine-containing halogen-adducts of tris(pentafluorophenyl)phosphine.

Since it has been clearly demonstrated in the preceding reactions that the bromotris(pentafluorophenyl)phosphonium and iodotris(pentafluorophenyl) phosphonium ions are formed in the reactions of tris(pentafluorophenyl) phosphine and halogens (Br_2, I_2, IBr), it was decided to investigate the possible existence of the analogous chlorophosphonium ion, $(C_6F_5)_3PCl^+$, in tetrahalides of the type $(C_6F_5)_3PCl_nHal_{4-n}$. The reactions of tris(pentafluorophenyl)phosphine with iodine chloride and iodine trichloride were therefore studied by conductometric titration and the conductance-composition graphs are reproduced in Fig. 11.

(a) $(C_6F_5)_3P/ICl$

This reaction appeared to occur very slowly, since after each addition of ICl to $(C_6F_5)_3P$ some time elapsed before the conductance attained a steady value (cf. the $(C_6F_5)_3P/I_2$ reaction). The solution had a colour characteristic of iodine in methyl cyanide from the first addition of iodine chloride. The conductance-composition graph shows an inflection at 2:1 (ICl: $(C_6F_5)_3P$) mole ratio, indicating that a reaction between 2 moles of iodine chloride and one of $(C_6F_5)_3P$ was taking place. However, the low molar conductance value at that point (Λ_m = 30.59 ohm.$^{-1}$ cm.^{2} mole.$^{-1}$; c_m = .009 mole/l) is not in keeping with formation of an ionic tetrahalide $(C_6F_5)_3PCl_2I_2$. The UV/visible spectra of the solution at the 2:1 mole ratio showed the presence of molecular iodine in considerable quantity. The formation of $(C_6F_5)_3PCl_2$ and iodine in solution according to the reaction (20) is thus suggested.

$$(C_6F_5)_3P + 2\ ICl \longrightarrow (C_6F_5)_3PCl_2 + I_2 \quad \text{.....(20).}$$

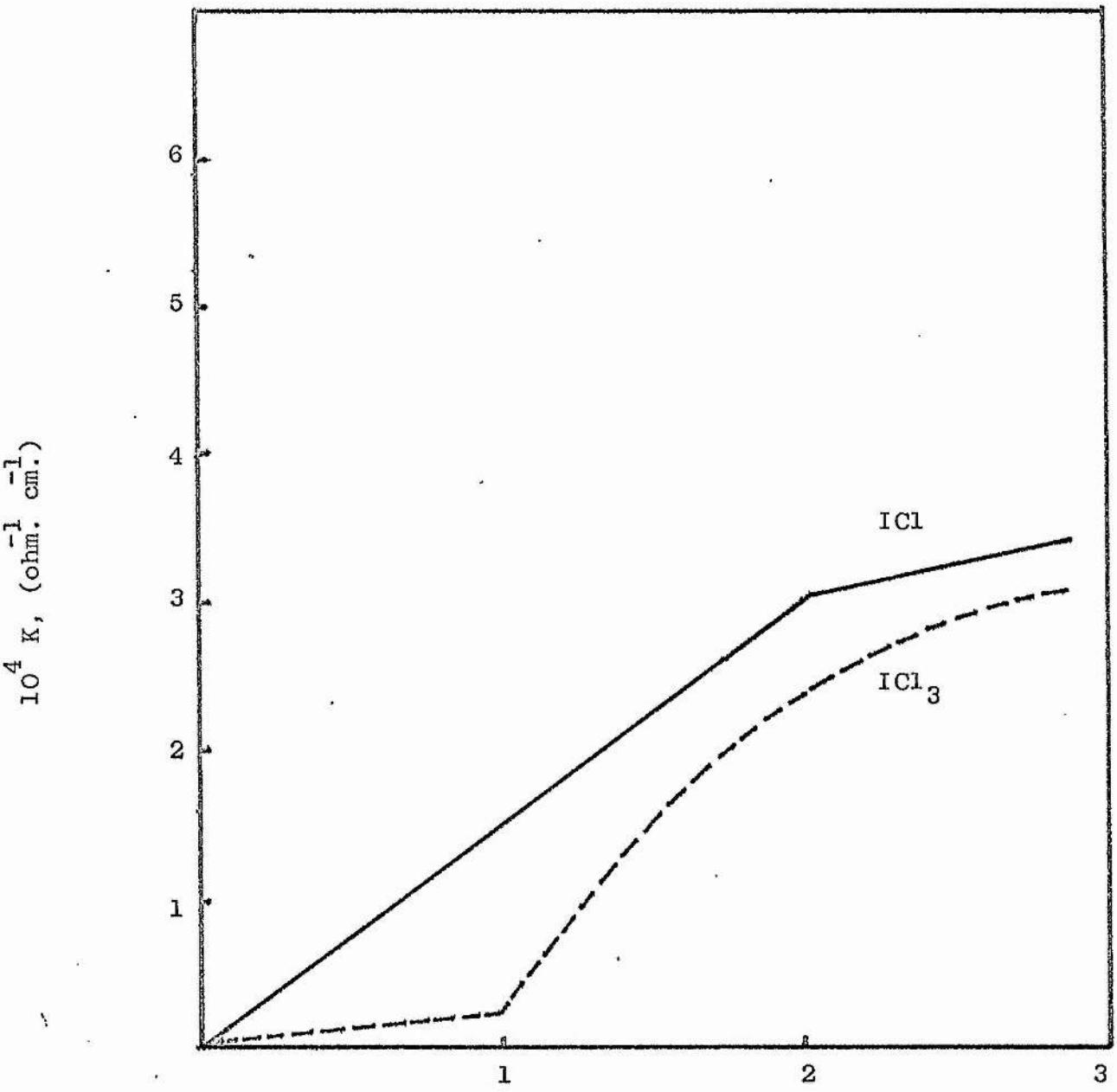


Fig. 11. Conductometric Analysis of the Systems Tris(pentafluorophenyl)phosphine-Halogens

In keeping with this, $(C_6F_5)_3PCl_2$ was isolated from the solution at this mole ratio.

To gain further support for the reaction (20), the stepwise reactions of $(C_6F_5)_3PCl_2$ with iodine and iodine chloride were examined by conductometric titrations. The conductance of the solution rose uniformly with the addition of halogen and there was no suggestion of an inflection in the graph; the rise in conductance can be attributed to the halogen itself. Also, $(C_6F_5)_3PCl_2$ was recovered from these solutions in each case. It is amply confirmed therefore that there is no reaction between $(C_6F_5)_3PCl_2$ and halogens under the conditions studied.

(b) $\underline{(C_6F_5)_3P/ICl_3}$:-

The reaction of $(C_6F_5)_3P$ and iodine trichloride was also found to be very slow and a conductance rise with time, similar to that in the $(C_6F_5)_3P/I_2$ and $(C_6F_5)_3P/ICl$ systems, was observed. Addition of ICl_3 to a solution of the phosphine in methyl cyanide produced a brownish-yellow coloured solution and the conductance rose only very slightly until the 1:1 (ICl_3: $(C_6F_5)_3P$) was reached. It then rose more rapidly corresponding exactly to that obtained on addition of ICl_3 to methyl cyanide alone. The molar conductance value at the 1:1 ratio was 21.37 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m, .0067mole/1., and $(C_6F_5)_3PCl_2$ was isolated from a solution containing $(C_6F_5)_3P$ and ICl_3 in equimolar amounts. The reaction is therefore:-

$$(C_6F_5)_3P + ICl_3 \longrightarrow (C_6F_5)_3PCl_2 + ICl.$$

These experiments therefore suggest the non-existence of the chlorine-containing halogen adducts, $(C_6F_5)_3PCl_nHal_{4-n}$, analogous to $(C_6H_5)_3MCl_nHal_{4-n}$ (M = P, As) described earlier.

(B) Tris(Pentafluorophenyl)arsine-Halogen Systems.

There is much evidence to show that the 'onium compounds of the group V elements, P, As, and Sb vary in their stability depending on the central element, the observed order being P > As > Sb. The same order is observed for the stability of molecular addition compounds of the alkyl and aryl derivatives of the hydrides of these elements. These trends are clearly tied up with the variation in the donor properties of the central atom as one goes down the series P, As, Sb.

From our study of tris(pentafluorophenyl)phosphine-halogen system it has been shown that replacement of the phenyl group with the electronegative pentafluorophenyl group considerably reduces the donor properties of the phosphorus atom, so that the system $(C_6F_5)_3P\text{-}Hal_2$ behaves more like the $(C_6H_5)_3As - Hal_2$ system. One can therefore predict that the pentafluorophenyl substituents in tris(pentafluorophenyl)arsine will also tend to affect considerably the donor properties of the arsenic atom so that the system $(C_6F_5)_3As - Hal_2$ might be expected to behave rather like $(C_6H_5)_3Sb - Hal_2$ system. Therefore the reactions of tris(pentafluorophenyl)arsine with some halogens were studied to obtain information on the effect of the strongly electronegative pentafluorophenyl group on the course of reactions and on the nature and stability of the products.

(1) Tris(pentafluorophenyl)arsenic dichloride:-

Tris(pentafluorophenyl)arsenic dichloride was prepared by the reaction of tris(pentafluorophenyl)arsine and chlorine in methyl cyanide.

The compound is a white crystalline solid (m.p. 214-216°), sparingly soluble in methyl cyanide, but readily soluble in ether, benzene, and other relatively non-polar organic solvents. Like its phosphorus analogue, tris(pentafluorophenyl)arsenic dichloride is readily hydrolysed to give the oxide, tris(pentafluorophenyl)arsine oxide; but, unlike triphenylarsenic dichloride there is no tendency to form a hydroxychloride and its oxide, $(C_6F_5)_3AsO$, does not form a monohydrate.[83]

The conductance of tris(pentafluorophenyl)arsenic dichloride was measured at 25° in methyl cyanide, and the molar conductance values (Table 15) which decreased with increasing concentration were of such a low value that tris(pentafluorophenyl)arsenic dichloride must be regarded as a non-electrolyte in this solvent.

Table 15. Conductance of Tris(pentafluorophenyl)arsenic dichloride in methyl cyanide

c_m mole/l	$K \times 10^4$ ohm.$^{-1}$cm.$^{-1}$	Λ_m ohm.$^{-1}$cm.^{2}mole.$^{-1}$
0.0026	0.023	0.914
0.0050	0.041	0.826
0.0076	0.058	0.760
0.0120	0.088	0.740
0.0144	0.099	0.690

(2) Reactions of Tris(pentafluorophenyl)arsine with Halogens.

(a) Reactions with Br_2, I_2 and IBr.

The conductometric titrations of halogens (Br_2, I_2, IBr) were carried out and the conductance-composition graphs each showed no inflection at any point. The observed slight rise in conductance corresponded to the addition of halogen itself to the pure solvent. Therefore, there is no evidence for the occurrence of any reaction. Also, tris(pentafluorophenyl)arsine was recovered from these solutions after addition of halogen.

(b) Reaction with Chlorine-Containing Interhalogens.

The reactions of tris(pentafluorophenyl)arsine with iodine chloride and iodine trichloride were studied using the conductometric method. The reaction was very similar to that of $(C_6F_5)_3P$ - Hal_2 (Hal_2 = ICl, ICl_3). The colourless arsine solution assumed the characteristic colour of the halogen after the first addition of titrant (ICl or ICl_3), and conductance graphs showed slight inflections at 2:1 for ICl and at 1:1 for ICl_3 titrations.

By analogy with the $(C_6F_5)_3P$/ICl or ICl_3 reactions, the following are occurring:-

$$(C_6F_5)_3As + 2\ ICl \longrightarrow (C_6F_5)_3AsCl_2 + I_2 \quad \ldots\ldots\ldots(21)$$

$$(C_6F_5)_3As + ICl_3 \longrightarrow (C_6F_5)_3AsCl_2 + ICl \quad \ldots\ldots\ldots(22)$$

The presence of iodine as a product of reaction (21) and of iodine chloride as a product of reaction (22) was confirmed from the U.V. spectrum of the respective solutions. Also, tris(pentafluorophenyl)arsenic dichloride was isolated from these reaction mixtures.

SUMMARY

The reactions of tris(pentafluorophenyl)phosphine and -arsine with halogens (Cl_2, Br_2, I_2) and interhalogens (IBr, ICl, ICl_3) have been studied. The only dihalides so far isolated are the dichlorides, $(C_6F_5)_3PCl_2$ and $(C_6F_5)_3AsCl_2$ which have been shown to behave as non-electrolytes in methyl cyanide solution. The formation of $(C_6F_5)_3PBr_2$, under suitable conditions in solution, has been indicated by conductometric titration of Br_2 and $(C_6F_5)_3P$; $(C_6F_5)_3PBr_2$ behaves as a weak electrolyte in methyl cyanide. The existence of two addition bromides of tris(pentafluorophenyl) phosphine, $(C_6F_5)_3PBr_{10}$ and $(C_6F_5)_3PBr_4$, has been demonstrated by vapour pressure studies of the $(C_6F_5)_3P$-Br_2 system. $(C_6F_5)_3PBr_4$ was isolated as a yellow, readily decomposable solid. From their properties, ionic structures $(C_6F_5)_3PBr^+ Br_3^-$ and $(C_6F_5)_3PBr^+ Br_9^-$ have been postulated for these compounds. Evidence has also been provided for the existence in solution of the following adducts of tris(pentafluorophenyl)phosphine - $(C_6F_5)_3PI_4$, $(C_6F_5)_3PI_2Br_2$, $(C_6F_5)_3PIBr_3$ etc. Attempted isolation of these as crystalline solids was not successful and gave only oily products. In solution the tetrahalides, $(C_6F_5)_3P\ Hal_4$ (Hal = Br or I), are strong 1:1 electrolytes and produce trihalide ions and $(C_6F_5)_3PBr^+$ or $(C_6F_5)_3PI^+$ ion. $(C_6F_5)_3As$ does not react with Br_2, I_2 and IBr under the conditions studied. With chlorine-containing interhalogens (ICl or ICl_3) both $(C_6F_5)_3As$ and $(C_6F_5)_3P$ react to produce their dichlorides. There is no evidence for the formation of a chlorine-containing tetrahalide.

PART III

HALOGEN ADDUCTS OF DIMETHYLAMINO -PHOSPHINES AND -ARSINES

I N D E X

INTRODUCTION

The aminohalophosphines $Hal_nP(NR_2)_{3-n}$ (R = alkyl group), which have been known for many years, are compounds which are characterized by the formal presence of a lone electron pair on the phosphorus atom and on each of the adjacent nitrogen atoms. Typical of this group of compounds is tris(dimethylamino)phosphine, which can be easily prepared from the action of phosphorus (111) halides on dimethylamine,[69] and whose reactions have been studied comprehensively by various workers.[103-106] It has been shown that in its reactions the phosphorus atom acts as the donor atom. The lack of basicity of the nitrogen atom in this and similar compounds can be attributed to the formation of d_π-p_π bonds involving a vacant d orbital of the phosphorus atom and the lone electron pair on the nitrogen atom. The latter are thus unavailable for donation to other groups.

Noth and Vetter have recently studied the reactions of tris(dimethylamino)phosphine with some halogens (Cl_2, Br_2, and I_2) and reported the formation of the dihalides, $(Me_2N)_3PHal_2$.[106] They have shown by conductance measurements in nitrobenzene that these dihalides are strong 1:1 electrolytes. The halo-tris(dimethylamino)phosphonium cation, $(Me_2N)_3PHal^+$ was identified by double salt formation with iron (111) chloride, and by reaction with $NaBPh_4$; the ionic structure, $(Me_2N)_3PHal^+\ Hal^-$, has thus been postulated for the solid state.

The formation of a tetrachloride, $(Me_2N)_3PCl_4$ has also been reported.[106]

Analogous aminoarsines, $Hal_nAs(NR_2)_{3-n}$ (n = 1 or 2) were described by Michaelis and Luxembourg in 1896.[107] Articles concerning this type of compound have been published occasionally since that time,[108,109] but it is only very recently that tris(dimethylamino)arsine has been prepared.[70] Tris(dimethylamino)arsine is a colourless liquid which decomposes in atmospheric moisture to dimethylamine and arsenic (lll) oxide. From its reactions with electrophilic reagents (e.g. HCl, PhCOCl, Ph_2BCl) it has been established that the As-N bond in $(Me_2N)_3As$ is much weaker than the P-N bond in $(Me_2N)_3P$, and cleavage of it occurs readily.[110]

The reactions of tris(dimethylamino)arsine with some halogens (Cl_2, Br_2, I_2) have been studied and the dihalides, $(Me_2N)_3AsCl_2$ and $(Me_2N)_3AsI_2$, reported to be stable only below 0^o.[110] However, the dibromide, $(Me_2N)_3AsBr_2$, has been isolated as a crystalline solid and on the basis of its solubility in methyl cyanide and nitrobenzene, and insolubility in petroleum ether, an arsonium salt structure, $(Me_2N)_3AsBr^+Br^-$ was proposed. The reaction of cyanogen bromide cleaves the As-N bond as follows.[110]

$$(Me_2N)_3As + BrCN \longrightarrow (Me_2N)_2AsBr + Me_2NCN$$

The corresponding antimony compounds, $Hal_nSb(NMe_2)_{3-n}$ have been reported to be very unstable.[111]

As part of our continuing interest in the halides of organophosphines, -arsines, and -stibines, a detailed study of some of the reactions of halogens and interhalogens with tris(dimethylamino)phosphine and -arsine was made. In this way it was hoped to obtain information about the way the strongly electron donating Me_2N group affected the nature of the reactions and the products.

RESULTS AND DISCUSSIONS

(A) The Tris(dimethylamino)phosphine-Halogen systems.

(1) Preparation and Stability of the Dihalides.

Tris(dimethylamino)phosphorus dichloride was prepared by the reaction of chlorine and tris(dimethylamino)phosphine in petroleum ether at -80°. Other dihalides [e.g. $(Me_2N)_3PBr_2$, $(Me_2N)_3PI_2$, $(Me_2N)_3PBrI$, $(Me_2N)_3PClI$] were obtained by mixing concentrated methyl cyanide solutions of the appropriate halogen and the phosphine.

Tris(dimethylamino)phosphorus dihalides are all high melting, moisture sensitive, solids, soluble in polar solvents (methyl cyanide, nitrobenzene) and insoluble in non-polar solvents (benzene, ether). The dihalides, in general, are moderately stable under nitrogen or under vacuum, but in atmospheric moisture they are readily hydrolysed to dimethylammonium halide and arsenious acid by the cleavage of the P-N bonds. On account of this the dihalides were prepared immediately before use and strict precautions, as in previous work involving similar organometallic halides, were taken to ensure the absence of moisture at all stages in their study.

(2) Electrolytic Conductance of the Dihalides.

Methyl cyanide was used as a solvent for the reasons mentioned earlier. The solutions were prepared in a dry box and the conductance measurements made over a range of concentration at 25°. The molar conductance values, which decrease with increasing concentration, are recorded in Table (16), overleaf. The high molar conductance values indicate that all of the dihalides are strong 1:1 electrolytes. By

Table (16) Electrolytic conductance of Tris(dimethylamino) phosphorus dihalides in methyl cyanide at 25°C

Dihalide	c_m (mole/l	$K \times 10^4$ (ohm.$^{-1}$cm.$^{-1}$)	Λ_m ohm.$^{-1}$cm.^{2}mole^{-1}	Λ_m at .01 mole/l
$(Me_2N)_3PCl_2$	.0021	2.39	114.0	88.50
	.0036	3.77	104.5	
	.0081	7.70	95.0	
	.0144	11.40	79.2	
	.0275	16.47	59.9	
$(Me_2N)_3PBr_2$	.0016	2.30	144.0	120.0
	.0045	6.01	135.1	
	.0126	13.75	110.0	
	.0193	20.00	103.5	
	.0264	25.20	95.5	
$(Me_2N)_3PI_2$	.0029	4.23	148.0	123.0
	.0054	7.35	136.0	
	.0088	11.00	125.0	
	.0123	14.20	115.5	
	.0167	17,65	105.9	
$(Me_2N)_3PICl$	.0049	6.89	139.5	127.0
	.0121	14.89	123.1	
	.0162	18.55	114.5	
	.0229	24.64	107.4	
	.0314	30.00	95.4	
$(Me_2N)_3PIBr$	.00479	6.80	142.2	129.0
	.0122	15.20	124.0	
	.0203	22.50	111.0	
	.0316	30.30	96.0	
	.0400	40.30	95.0	

analogy with Ph_3PHal_2, the behaviour of $(Me_2N)_3PHal_2$ in methyl cyanide is thus:-

$$(Me_2N)_3PHal_2 \longrightarrow (Me_2N)_3PHal^+ + Hal^-.$$

A similar behaviour in nitrobenzene has been observed.[106] Comparison of the molar conductance values of .01M solutions of the tris(dimethylamino) phosphorus dihalides with triphenylphosphorus dihalides reveals that the values are slightly higher for the dimethylamino compounds.

(3) Conductometric titration studies of $(Me_2N)_3P$-Hal_2 Systems.

(a) Reactions with Br_2, I_2 and IBr

The shape of the conductance-composition graphs obtained in these systems were remarkably similar and each had breaks at the 1:1 and 2:1 (Hal_2: $(Me_2N)_3P$) mole ratios, (Fig. 12). In each, the solution was colourless up to the 1:1 ratio, but thereafter had the dark colour indicative of trihalide ion. The slight conductance increase after the 2:1 ratio was attributable to the addition of halogen to a strong conducting solution when reaction does not occur. The reactions occurring in solution can therefore be written as follows.

$$(Me_2N)_3P + Br_2 \longrightarrow (Me_2N)_3PBr^+.\ Br^- \xrightarrow{+Br_2} (Me_2N)_3PBr^+.Br_3^-$$

$$(Me_2N)_3P + I_2 \longrightarrow (Me_2N)_3PI^+I^- \xrightarrow{+\ I_2} (Me_2N)_3PI^+\ I_3^-$$

$$(Me_2N)_3P + IBr \longrightarrow (Me_2N)_3PBr^+\ I^- \xrightarrow{+\ IBr} (Me_2N)_3PBr^+I_2Br^-$$

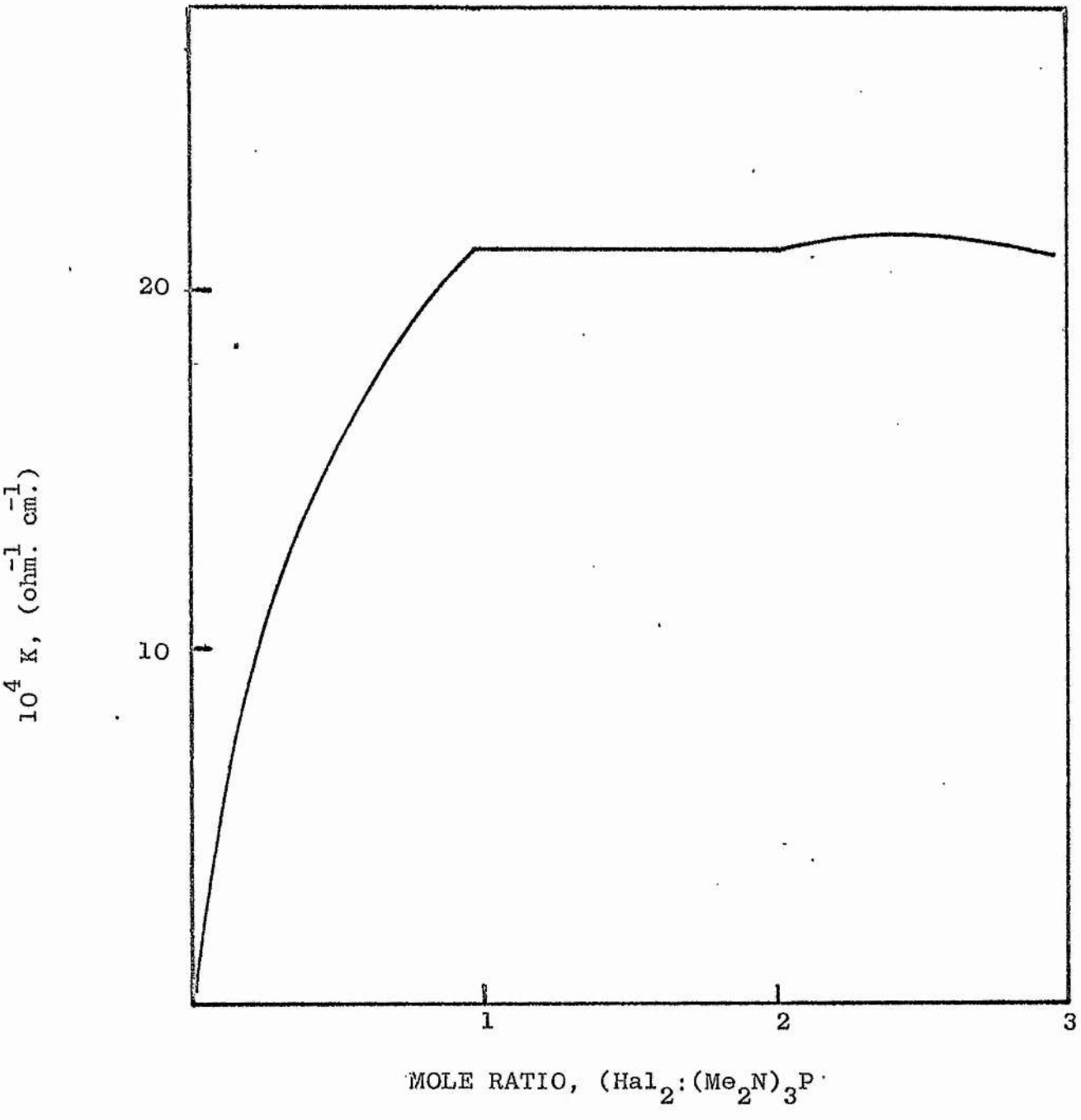


Fig. 12. Conductometric Analysis of the Systems Tris(dimethylamino)phosphine-Halogens

(b) Adducts isolated:-

All of the dihalides whose existence was shown by conductometric titration and some of the tetrahalides (n = 0, 2, and 4) of the series $(Me_2N)_3PI_nBr_{4-n}$ were isolated as crystalline solids by addition of ether to the methyl cyanide solution of the reactants in the appropriate ratios. The compounds with n = 3 and 1 were obtained from reactions

$$(Me_2N)_3PIBr + I_2 \longrightarrow (Me_2N)_3PI_3Br$$

$$(Me_2N)_3PIBr + Br_2 \longrightarrow (Me_2N)_3PIBr_3.$$

Confirmation of the presence of a phosphonium-type of structure, $(Me_2N)_3PHal^+$, rather than ammonium in these compounds was obtained from their infra-red spectra. It is known that a methyl group bonded to a nitrogen atom which bears a lone pair of electrons, $>\ddot{N}$ Me, gives rise to a characteristic symmetric C-H stretching frequency in the 2760-2820 $cm.^{-1}$ region (at 2810 $cm.^{-1}$ in $(Me_2N)_3P$); if the lone pair electron is tied up by co-ordination (e.g. in Me_4NCl) this absorption is absent.[112,113] In infra-red spectra of all of the adducts obtained in the present work, absorption occurs in this region thus providing strong evidence for the bonding through phosphorus.

The properties of these crystalline adducts are summarised in Table (17). The dibromide and the di-iodide have been reported before.[106]

Table (17) Crystalline adducts of $(Me_2N)_3P$ with Halogens

Compound	Colour	m.p. °C	Λ_m ohm.$^{-1}$ cm.^{2} mole.$^{-1}$ at 25° (c_m = .01 mole/l)
$(Me_2N)_3PBr_2$	Yellow	246-248	120.0
$(Me_2N)_3PI_2$	Yellow	240-247	123.0
$(Me_2N)_3PIBr$	White	224-226	129.0
$(Me_2N)_3P\ Br_4$	Orange	90-92	136.0
$(Me_2N)_3PBr_3I$	Red orange	94-96	130.0
$(Me_2N)_3PBr_2I_2$	Red	88-89	122.0
$(Me_2N)_3PBrI_3$	Red	103-104	131.0
$(Me_2N)_3PI_4$	Chocolate	89-90	123.8

(4) Chlorine-containing Halogen Adducts of Tris(dimethylamino)phosphine.

(a) Reaction of Tris(dimethylamino)phosphine with Chlorine.

Tris(dimethylamino)phosphine has been shown to react with chlorine to form a tetrachloride $(Me_2N)_3PCl_4$, and an ionic structure containing a trichloride ion, $(Me_2N)_3PCl^+.Cl_3^-$, suggested.[106] The only other compound of the trichloride ion is $Et_4N\ Cl_3$ reported by Chattaway & Hoyle.[114] Since the existence of a trichloride ion in solid and solution is not very well established, it was of interest to obtain further evidence for its existence. Therefore the reaction of tris(dimethylamino)phosphine and chlorine was studied by stepwise addition of chlorine to the phosphine

in methyl cyanide and following any change conductometrically. The conductance of the solution was found to rise steeply with the addition of chlorine up to the 1:1 ratio, during which the solution remained colourless. From the 1:1 to the 2:1 (Cl_2: $(Me_2N)_3P$) ratio the solution acquired a pale yellow colour and the conductance rose slowly but significantly and after 2:1 ratio the conductance gradually fell off. For a comparison the conductance-composition graphs for the systems $(Me_2N)_3P/Cl_2$ and Ph_3P/Cl_2 are reproduced in Figure (13). The conductance-composition graph in the latter case shows no rise in specific conductance beyond 1:1 ratio. The rise in conductance after the 1:1 ratio in the $(Me_2N)_3P/Cl_2$ reaction along with the higher molar conductance value at 2:1 ratio

$$1{:}1 \quad \Lambda_m = 56.20 \text{ ohm.}^{-1}\text{cm.}^{2}\text{mole.}^{-1} \quad (c_m = .022 \text{ mole/l})$$

$$2{:}1 \quad \Lambda_m = 78.60 \text{ ohm.}^{-1}\text{cm.}^{2}\text{mole.}^{-1} \quad (c_m = .022 \text{ mole/l})$$

was taken as a good evidence for the formation of tris(dimethylamino) phosphorus tetrachloride in solution.

$$(Me_2N)_3P + Cl_2 \longrightarrow (Me_2N)_3PCl_2 \xrightarrow{+\,Cl_2} (Me_2N)_3PCl_4$$

$$(Me_2N)_3PCl^+\ Cl^- \qquad (Me_2N)_3PCl^+\ Cl_3^-$$

In keeping with this, $(Me_2N)_3PCl_2$ and $(Me_2N)_3PCl_4$ were isolated from the solutions containing 1:1 and 2:1 mole ratios of Cl_2 and $(Me_2N)_3P$.

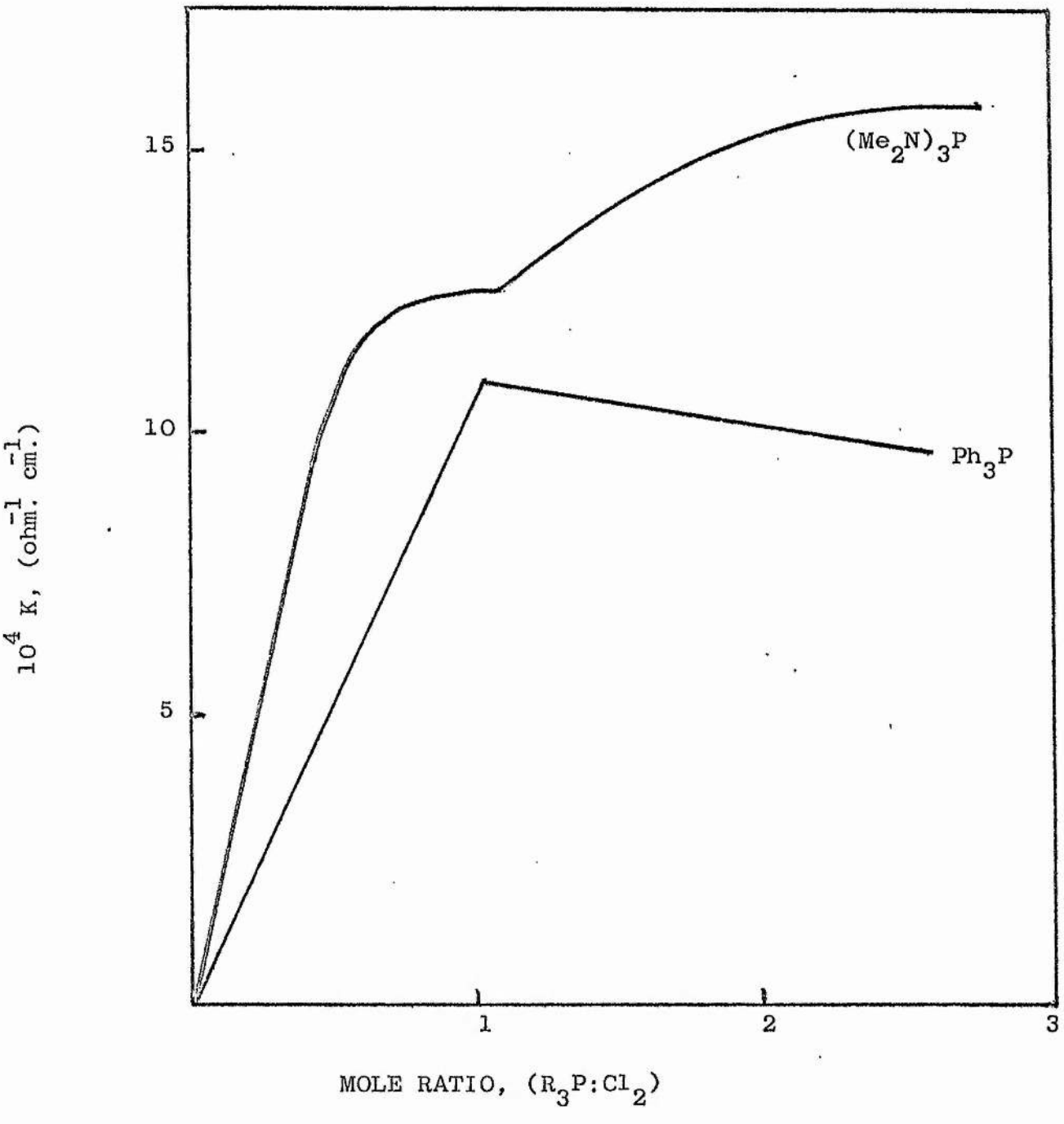


Fig. 13. Conductometric Titrations of R_3P with chlorine in Methyl cyanide

(b) Reaction of Tris(dimethylamino)phosphine with Iodine Chloride and Iodine Trichloride

(i) $(Me_2N)_3P/ICl$

Unlike the triphenylphosphine-iodine chloride reaction which has unexpected conductance properties and which produces rather complicated reaction products, the $(Me_2N)_3P/ICl$ reaction is fairly straight forward. The conductance-composition graph was similar to that obtained from the $(Me_2N)_3P$-Hal_2 (Hal_2 = Br_2, I_2, IBr) systems already studied. The breaks in the graph at 1:1 and 2:1 mole ratios were taken as indicating the formation in solution of the dihalide $(Me_2N)_3P\,ICl$ and the tetrahalide $(Me_2N)_3PI_2Cl_2$ by the reaction:-

$$(Me_2N)_3P + ICl \longrightarrow \underset{\underset{(Me_2N)_3P\overset{+}{C}l\ I^-}{\updownarrow}}{(Me_2N)_3PICl} \xrightarrow{ICl} \underset{\underset{(Me_2N)_3PCl^+\ I_2Cl^-}{\updownarrow}}{(Me_2N)_3PI_2Cl_2}$$

In accord with this $(Me_2N)_3PClI$ and $(Me_2N)_3PCl_2I_2$ were isolated as crystalline solids from solutions of ICl and $(Me_2N)_3P$ in the appropriate proportions.

(ii) $(Me_2N)_3P/ICl_3$

The conductance-composition graph for the titration of iodine trichloride with tris(dimethylamino)phosphine is illustrated in Figure (14). The breaks in the graph at the 0.5:1 and 1:1 (ICl_3:$(Me_2N)_3P$) mole ratios corresponded to the formation of the dihalides and tetrahalide

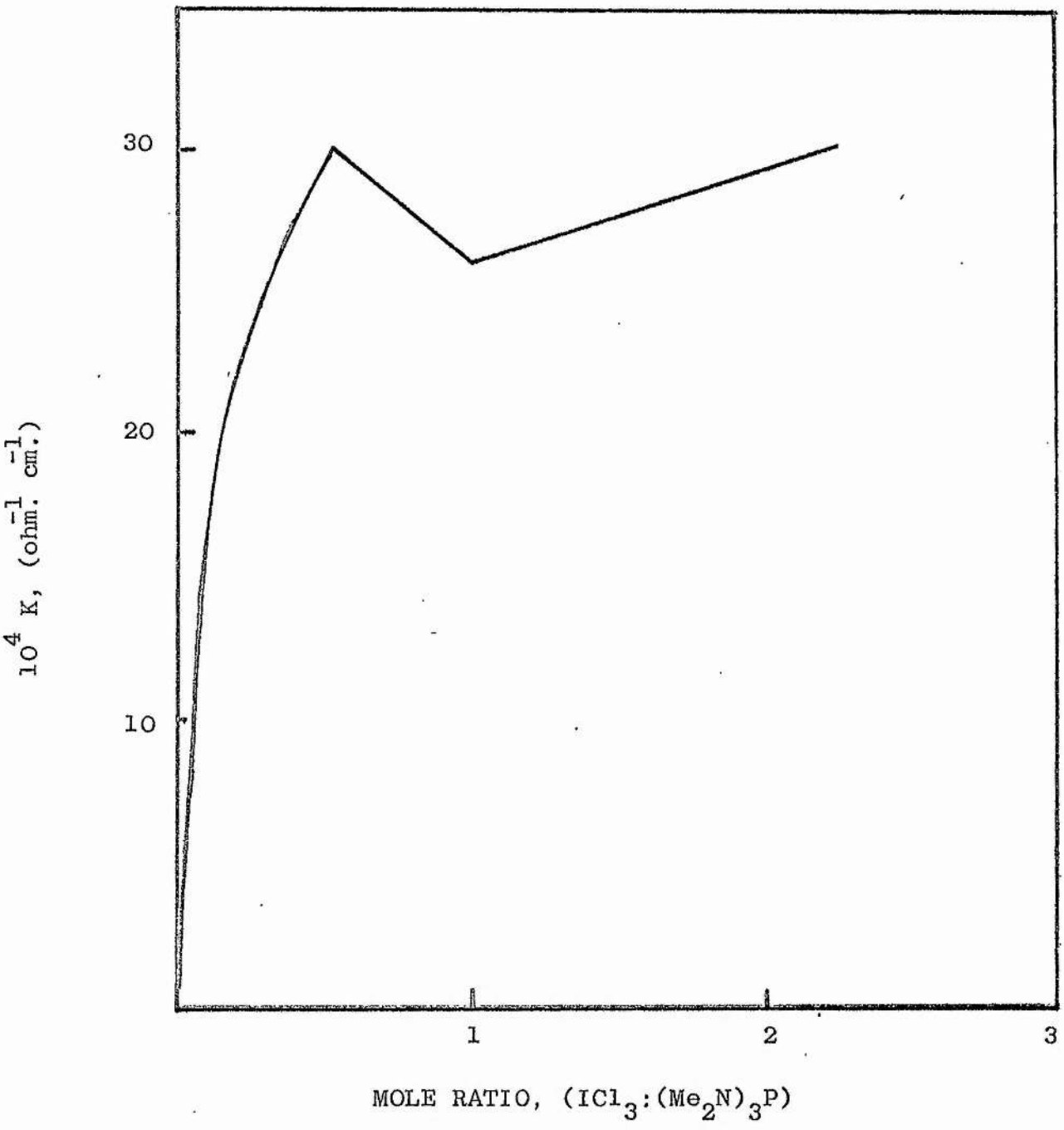


Fig. 14. Conductometric Analysis of the System Tris(dimethylamino)phosphine-Iodine trichloride

according to the following equations:-

$$(0.5{:}1 \text{ ratio}) \quad 2\,(Me_2N)_3P + ICl_3 \longrightarrow \underbrace{(Me_2N)_3PICl + (Me_2N)_3PCl_2}$$

$$\downarrow +ICl_3 (\equiv Cl_2 + ICl)$$

$$(1{:}1 \text{ ratio}) \qquad (Me_2N)_3PICl_3 + (Me_2N)_3PICl_3.$$

The solution remained colourless up to the 0.5:1 mole ratio, and thereafter had the bright yellow colour of the ICl_2^- ion. Solid $(Me_2N)_3PICl$ and $(Me_2N)_3PICl_3$ were isolated from the solutions at 0.5:1 and 1:1 mole ratios respectively.

(iii) Adducts isolated:-

As mentioned earlier the dihalides $(Me_2N)_3PCl_2$ and $(Me_2N)_3PICl$ have been isolated, and in the case of the tetrahalides, each compound in the series $(Me_2N)_3P\ I_nCl_{4-n}$ has been prepared. The tetrachloride (n = 0) was obtained by the reaction of $(Me_2N)_3P$ and dry chlorine in a suitable solvent (methyl cyanide) at $-30^{\circ}C$. $(Me_2N)_3PCl_2I_2$ (n = 2) and $(Me_2N)_3PCl_3I$ (n = 1), were isolated by addition of ether to a methyl cyanide solution containing phosphine and ICl, ICl_3, in the appropriate ratios, and the compound with n = 3, $(Me_2N)_3PI_3Cl$, was obtained from the reaction:-

$$(Me_2N)_3PICl + I_2 \longrightarrow (Me_2N)_3PI_3Cl.$$

Some properties of these crystalline adducts are summarised in Table (18) overleaf., Except for the dichloride and tetrachloride, none of these halides has been reported before.

Table (18) Crystalline Adducts of $(Me_2N)_3P$ with Halogens

Compound	Colour	m.p. °C	Λ_m ohm.$^{-1}$cm.^{2}mole.$^{-1}$ at 25°, (c_m = .01mole/l)
$(Me_2N)_3PCl_2$	White	266-270	88.5
$(Me_2N)_3PClI$	White	226-235	127.0
$(Me_2N)_3PCl_4$	Yellow	75-80	138.0
$(Me_2N)_3PCl_3I$	Yellow	103-104	130.5
$(Me_2N)_3PCl_2I_2$	Red Yellow	76-78	130.0
$(Me_2N)_3PClI_3$	Red .	104	124.5
$(Me_2N)_3P\ I_4$	Chocolate	89-90	123.8

(B) The Tris(dimethylamino)arsine-Halogen Systems.

Because of the extreme sensitivity of tris(dimethylamino)arsine towards oxygen and moisture it was found to be not possible to do conductometric titration studies of all the $(Me_2N)_3As$-Hal_2 systems by the general technique used in the study of other systems. However, it was possible to carry out a conductometric study of the systems $(Me_2N)_3As/Cl_2$ and $(Me_2N)_3As/Br_2$ in a specially designed vacuum system, by stepwise addition of small amounts of chlorine or bromine vapour to a methyl cyanide solution of tris(dimethylamino)arsine. The stability of methyl cyanide as a solvent was established by the recovery of the arsine after standing in methyl cyanide for a long time.

(1) $(Me_2N)_3As/Cl_2$

On adding chlorine to a solution of the arsine solution contained in a conductivity cell, considerable heat was evolved and the solution acquired a dark brown colour thus indicating the breakdown of the product under these conditions. Therefore, it was decided to repeat the reaction at -35°, as $(Me_2N)_3AsCl_2$ has been reported to be stable at low temperatures.[110] In this case the solution remained colourless and the conductance of the arsine solution rose uniformly as chlorine was added from its near zero value at the beginning until the 1:1 ratio was reached. After that there was no significant change in conductance. The formation of the 1:1 adduct $(Me_2N)_3AsCl_2$ at $-35^{\circ}C$ was thus indicated.

$$(Me_2N)_3As + Cl_2 \longrightarrow (Me_2N)_3AsCl_2$$

The low molar conductance (Λ_m = 5.97 ohm.$^{-1}$cm.^{2}mole.$^{-1}$, c_m = .021 mole/l) at 1:1 ratio suggested that the dichloride is a weak electrolyte at -35°C. However, in order to obtain a value for the conductance which could be compared with those of other dihalides the specific conductance of a .01M solution of $(Me_2N)_3AsCl_2$ was measured in the range -35° to 0° and the graph Λ_m against temperature was extrapolated to 25°. The molar conductance value obtained by extrapolation was 27.5 ohm.$^{-1}$cm.^{2}mole.$^{-1}$ thus confirming the weak electrolytic character of this compound in methyl cyanide.

(2) $(Me_2N)_3As/Br_2$

The system $(Me_2N)_3As$-Br_2 resembled closely the $(Me_2N)_3P$-Br_2 system, discontinuities at the 1:1 and 2:1 (Br_2: $(Me_2N)_3As$) mole ratios indicating the formation of the adducts $(Me_2N)_3AsBr_2$ and $(Me_2N)_3AsBr_4$. The solution was colourless up to the 1:1 ratio and thereafter had the bright yellow colour of the tribromide ion. The high molar conductance values at 1:1 and 2:1 for the relatively high concentration used

1:1 Λ_m = 45.70 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .031 mole/l,

2:1 Λ_m = 48.40 ohm.$^{-1}$cm.^{2}mole.$^{-1}$; c_m = .031 mole/l,

indicate that these adducts are strong 1:1 electrolytes.

$$(Me_2N)_3As + Br_2 \longrightarrow (Me_2N)_3AsBr_2 \xrightarrow{+\,Br_2} (Me_2N)_3AsBr_4$$

$$(Me_2N)_3AsBr_2 \rightleftharpoons (Me_2N)_3AsBr^+Br^- \qquad (Me_2N)_3AsBr_4 \rightleftharpoons (Me_2N)_3AsBr^+Br_3^-$$

(3) Reaction of $(Me_2N)_3As$ with interhalogens (IHal = IBr, ICl, ICl_3)

As mentioned earlier these reactions could not be studied by the usual technique of conductometric titration; however, attempts were made to isolate the mixed dihalides, $(Me_2N)_3AsIBr$ and $(Me_2N)_3AsICl$, and tetrahalides, $(Me_2N)_3AsI_2Br_2$, $(Me_2N)_3AsI_2Cl_2$, $(Me_2N)_3AsICl_3$, by ether precipitation from methyl cyanide containing appropriate mole ratios of halogen and arsine:

$$(Me_2N)_3As + IBr \longrightarrow (Me_2N)_3AsIBr \xrightarrow{+IBr} (Me_2N)_3AsI_2Br_2$$

$$(Me_2N)_3As + ICl \longrightarrow (Me_2N)_3AsICl \xrightarrow{+ICl} (Me_2N)_3AsI_2Cl_2$$

$$(Me_2N)_3As + ICl_3 \longrightarrow (Me_2N)_3AsICl_3.$$

Solid compounds crystallised out in each case but it was found that these were in fact tetrakis(dimethylamino)arsonium trihalides, the anion being that expected for the simple 2:1 adduct anticipated. These tetrakis-arsonium trihalides were amply characterised by their elemental analysis, their U.V. spectra in methyl cyanide solution, and by comparison of their infra-red spectra with those of authentic samples of $[(Me_2N)_4As]Cl$ and $[(Me_2N)_4As]I_2Cl$ which were synthesised for this purpose.

The rapid migration of Me_2N group in these reactions as distinct from those of $(Me_2N)_3P$ was very unexpected. To account for this one has to take into consideration the relative strength of the As-N and P-N bonds. All the evidence points to the former being considerably

weaker than the latter,[70,110] for example in the reaction of tris(dimethylamino)arsine and cyanogen bromide, $(Me_2N)_2AsBr$ and Me_2NCN are reported to be formed due to easy cleavage of the As-N bond. By analogy with this the following may be considered as the first stage in the reaction of $(Me_2N)_3As$ and interhalogens.

$$(Me_2N)_3As + IHal \longrightarrow (Me_2N)_2AsI + Me_2NHal \quad .....(23)$$

Again, it has been shown that $(Me_2N)_3As$ readily undergoes an addition reaction with Me_2NHal (Hal = Cl, Br) to form a stable quaternary compound $[(Me_2N)_4As]Hal$.[110] It would seem quite likely that as the reaction (23) proceeds the Me_2NHal formed reacts with unreacted $(Me_2N)_3As$ to produce $(Me_2N)_4As\ Hal$

$$(Me_2N)_3As + Me_2NHal \longrightarrow [(Me_2N)_4As]Hal \quad .....(24)$$

and on further addition of halogen the trihalide of tetrakis(dimethylamino)arsonium salt is formed. Thus the overall reactions occurring in solution can be written as:-

$$2\ (Me_2N)_3As + 2\ IBr \longrightarrow (Me_2N)_4As^+\ I_2Br^- + (Me_2N)_2AsBr$$

$$2\ (Me_2N)_3As + 2\ ICl \longrightarrow (Me_2N)_4As^+\ I_2Cl^- + (Me_2N)_2AsCl$$

$$2\ (Me_2N)_3As + ICl_3 \longrightarrow (Me_2N)_4As^+\ ICl_2^- + (Me_2N)_2AsCl$$

The properties of the crystalline adducts isolated from $(Me_2N)_3As$ - halogen reactions are summarised in Table (19).

Table (19) Crystalline Adducts of $(Me_2N)_3As$ with Halogens

Compound	Colour	m.p. °C	Λ_m ohm.$^{-1}$cm.^{2}mole.$^{-1}$ at 25° (c_m = .01 mole/l)
$(Me_2N)_3AsBr_2$	Pale Yellow	109.0	109.0
$(Me_2N)_3AsBr_4$	Orange Yellow	137.0	137.0
$[(Me_2N)_4As]I_2Br$	Red	91-93	138.0
$[(Me_2N)_4As]I_2Cl$	Red	88-92	131.0
$[(Me_2N)_4As]ICl_2$	Yellow	102-105	128.5

SUMMARY

Tris(dimethylamino)phosphine has been shown to react with halogens (Cl_2, Br_2, I_2) and interhalogens (ICl, IBr, ICl_3) to form simple 1:1 adducts (e.g. $(Me_2N)_3PCl_2$, $(Me_2N)_3PClI$) and the 1:2 adducts, $(Me_2N)_3PCl_nI_{4-n}$ (n = 0 to 4) and $(Me_2N)_3PBr_nI_{4-n}$ (n = 0 to 4). Conductometric titration of the $(Me_2N)_3P$-Cl_2 system in methyl cyanide gave clear indication of the formation of the trichloride ion in solution. The conductance of methyl cyanide solutions of the dihalides and tetrahalides has been measured and the molar conductance values compared with those of the corresponding triphenylphosphine compounds. All of the 1:1 and 1:2 adducts are strong electrolytes and ionise as halogenotris(dimethylamino)phosphonium salts.

The reaction of tris(dimethylamino)arsine with halogens and interhalogens has also been examined. The only adducts of tris(dimethylamino)arsine which are stable at normal temperatures are the dibromide, $(Me_2N)_3AsBr_2$, and tetrabromide, $(Me_2N)_3AsBr_4$; the dichloride, $(Me_2N)_3AsCl_2$ is stable at -35°. The formation of a di-iodide and tetraiodide is not very pronounced. Interhalogens (ICl, IBr, ICl_3) have been shown to cleave an As-N bond in $(Me_2N)_3As$ and the crystalline compounds isolated were tetrakis(dimethylamino)arsonium trihalides.

APPENDIX

INFRARED SPECTRA

The infrared spectra of the halogen adducts of the organosubstituted phosphines, -arsines, and -stibines, reported in the present work, were measured in the region 4000-200 $cm.^{-1}$ using a Perkin-Elmer model 621 grating spectrophotometer. All of the compounds were mounted as mulls in nujol or Kel-F No.3 fluorocarbon oil held between caesium iodide plates. Documentation of the spectral bands is presented and the salient features discussed in the following sections.

(1) Halogen adducts of Ph_3M (M = P, As or Sb)

Ph_3M may be regarded as a derivative of benzene, with the single substituent Ph_2M in the ring, so that vibrational assignments can be made for all the observed bands by comparison with monosubstituted benzenes and the vibrations due to the central skeleton of the molecule may be neglected. Deacon et.al.[115] and Sharp et.al.[116] have made a detailed study of the phenyl derivatives of the phosphorus group elements and have shown that all absorptions in the infrared spectra of these compounds may be assigned by comparison with Whiffen's assignments for the halobenzenes.[117]

The pure dihalides, $Ph_3M\ Hal_2$, and tetrahalides, $Ph_3M\ Hal_4$, are transparent in the region 4000-1600 $cm.^{-1}$ (except for C-H, ca. 3070 $cm.^{-1}$, and overtones of phenyl vibrations). Jensen and Nielsen have reported that Ph_3AsCl_2 and Ph_3AsBr_2 absorb strongly in the region 3000-2290 $cm.^{-1}$ [118], but this has recently been shown by Harris and Inglis to be due to the presence of $Ph_3AsOHCl$ and $Ph_3AsOHBr$, formed by the hydrolysis of the dihalides.[83]

The infrared spectra in the region 1600-200 $cm.^{-1}$ of the halogen adducts of Ph_3M prepared in the course of this work are recorded in Table 20.

Table 20. Infrared Spectra of Ph_3M-Hal_2 adducts

Ph_3PCl_2. 1580(w), 1477(m), 1435(s), 1322(vw), 1307(w), 1178(vw), 1155(vw), 1118(m), 1110(m), 1096(s), 1072(w), 1023(w), 993(m), 740(s,br), 725(s), 690(s), 617(w), 580(m-s), 535(s), 515(m), 495(m), 445(m,br).

Ph_3PClI. 1580(w), 1477(m), 1435(s), 1330(vw), 1307(w), 1178(vw), 1156(vw), 1119(m), 1110(m), 1097(s), 1072(w), 1023(w), 992(m), 740(m), 725(vs), 719(vs), 690(vs), 617(vw), 580(m), 535(s), 515(m), 499(m), 445(m,br).

Ph_3PCl_3I. 1580(w), 1477(m), 1435(s), 1325(vw), 1305(vw), 1178(vw), 1155(vw), 1115(m), 1097(s), 1072(w), 1023(m), 990(m), 740(m), 725(s), 720(s), 690(s).

$[(Ph_3P)_2Cl]I_3$. 1580(m), 1477(m), 1435(s), 1325(vw), 1305(vw), 1178(w), 1155(w), 1120(vw), 1110(m), 1097(s), 1070(w), 1022(w), 992(m), 740(s), 725(s), 720(vs), 690(vs), 615(w), 580(m), 535(m), 515(s), 504(s), 497(s), 443(m).

$[(Ph_3P)_2Br]I_3$. 1579(w), 1477(m), 1435(s), 1325(vw), 1305(vw), 1178(vw), 1155(w), 1120(w), 1110(m), 1097(m), 1022(w), 992(m), 740(s), 725(vs), 690(vs), 615(w), 535(m), 517(s), 505(s), 497(s), 490(m,sh), 442(m).

$[(Ph_3P)_2Br]HgBr_3$. 1580(w), 1476(m), 1435(s), 1325(vw), 1305(vw), 1178(vw), 1155(vw), 1120(s), 1110(m), 1097(m), 1022(w), 992(w), 740(s), 727(vs), 690(vs), 615(w), 537(s), 515(s), 496(vs), 490(m,sh), 442(m).

Ph_3PBr_2. 1580(w), 1475(m), 1438(s), 1326(vw), 1306(vw), 1178(vw), 1155(vw), 1120(s), 1108(m), 1097(m), 1020(w), 992(m), 750(s), 729(vs), 690(vs), 615(w), 535(vs), 510(m), 499(s), 490(s,sh), 441(m).

Table 20 cont. Infrared Spectra of $Ph_3M\text{-}Hal_2$ adducts

Ph_3AsCl_3I. 1576(m), 1475(m), 1439(s), 1330(vw), 1310(w), 1280(vw), 1159(w), 1084(m), 1020(w), 997(s), 740(vs), 690 doublet(vs), 610(w), 470(s), 365(s), 345(m-s), 328(w), 241(m,br).

$Ph_3AsCl_5I_2$. 1578(m), 1475(m), 1438(s), 1330(w), 1310(w), 1280(vw). 1160(w), 1084(m), 1020(w), 997(m-s), 740(vs), 690(vs).

$Ph_3AsClBr_2I$. 1575(m), 1475(m), 1438(s), 1330(w), 1310(w), 1280(vw), 1160(w), 1083(m), 1020(m), 999(m-s), 740(vs), 689(vs), 610(vw), 480(vs), 470(vs), 440(m), 360(s), 345(s), 328(w), 240(m,br).

$(Ph_3AsOH^+)_2Cl^-\ ICl_2^-$. 3000-2290(s,br), 1580(m), 1480(m), 1435(s), 1330(w), 1310(w), 1280(vw), 1160(w), 1083(m), 1020(w), 999(m-s), 780(m), 760(s), 740(vs), 687(vs).

Ph_3SbClI. 1580(w), 1480(m), 1440(s), 1325(m), 1300(vw), 1260(vw), 1175(w), 1157(m), 1052(m), 1012(m), 992(s), 727(vs), 680(vs).

$(Ph_3SbI)_2O$. 1580(w), 1480(m), 1436(s), 1325(m), 1303(w), 1260(vw), 1175(w), 1155(w), 1052(m), 1012(m), 992(s), 905(m), 760(vs), 730(vs), 684(vs).

In general, the spectra of the $Ph_3M\text{-}Hal_2$ adducts are alike and all the absorptions may be allocated to the normal vibrations of the aromatic ring in monosubstituted benzene. Slight shifts in band positions may be attributed to the mass effect of the central atom: this has been observed in the case of Ph_3M by other workers.[118,119] Only those planar ring vibrations of monosubstituted benzene which have been described as X-sensitive vibrations (Whiffen's (q) and (r) modes) are dependent on the nature of the substituent; and these move to a lower frequency as

the electronegativity of the substituent decreases (P>As>Sb).[119] These were observed at about 1108 and 720 $cm.^{-1}$ for phosphorus, about 1083 and 690 $cm.^{-1}$ for arsenic, and about 1052 for antimony compounds.

The following vibrational assignments are made by comparison with the published work on similar compounds.[115,116,118]

The three bands in the region 1600-1400 $cm.^{-1}$ (1584 ± 3 (w-m), 1481 ± 4 (m), and 1437 ± 4 (s) $cm.^{-1}$) may be assigned to C-C stretching vibrations, the bands at 1180 ± 6 (w), 1157 ± 3 (w-m), 1027 ± 5 (w-m) and ca. 1070(w) $cm.^{-1}$ are probably due to C-H in plane deformation modes, the band at 995 ± 4 (w) $cm.^{-1}$ to the phenyl breathing mode, and the bands at 740(s), 687 ± 3 (vs) $cm.^{-1}$ to the CH out of plane deformation modes.

For the absorptions below 650 $cm.^{-1}$, Whiffen has shown that the C-X vibrations of mono-substituted benzenes are coupled with ring vibrations and no specific bands can be assigned to C-X stretching vibration.[117] Sharp and co-workers agree with this view and have shown that the principal absorptions in the region 625-200 $cm.^{-1}$ (for Ph_3M) can all be assigned simply as those of a mono-substituted benzene.[116] Thus for Ph_3P and Ph_3As they observed Whiffen's X-sensitive (t) modes at 418, 429 $cm.^{-1}$ and 305, 311 $cm.^{-1}$ and the (y) modes (involving Ph-M out of plane deformation) at 494, 510 $cm.^{-1}$ and 470 $cm.^{-1}$ respectively.[116] The analogous bands in the above recorded samples are probably the 535, 445 $cm.^{-1}$ ones for phosphorus, and 470, 328 $cm.^{-1}$ for arsenic compounds. Some workers have assigned these bands to the M-C asymmetric and symmetric stretching vibrations respectively.[118,73]

All of the chlorine-containing halogen adducts of triphenylphosphine showed an absorption at 580(m-s)$cm.^{-1}$ which was absent in the bromo compounds and this we attribute to the P-Cl stretching vibration. A shoulder at 490 $cm.^{-1}$ in the bromo compounds (absent in chloro compounds) is probably the P-Br stretching frequency. Both ν P-Cl and ν P-Br vibrations lie at the upper end of the stretching frequencies usually assigned to these bonds.[120,121] An absorption at ca. 240(m,br)$cm.^{-1}$ observed in chloro compounds of Ph_3As is tentatively assigned to As-Cl stretch. A similar low As-Cl stretching vibration has been observed in Ph_3AsCl_2.[50]

(2) Halogen adducts of $(C_6F_5)_3M$

The infrared spectra of the perfluorophenyl compounds of phosphorus and arsenic in the range 4000-200 $cm.^{-1}$ are summarised in Table (21), and the following vibrational assignments are made by comparison with the recently published work of Glemser and co-workers on pentafluorophenyl-phosphorus compounds.[98]

Table 21. Infrared Spectra of $(C_6F_5)_3M\text{-}Hal_2$ adducts

$(C_6F_5)_3P$. 1650(s), 1560(w), 1522(vs), 1486(vs), 1392(s), 1296(s), 1285(sh), 1250(w), 1145(m), 1095(vs), 1080(sh), 1030(m), 980(vs), 850(m), 840(w), 826(vw), 765(m), 752(m), 728(m), 670(w), 660(w), 640(m), 624(m), 587(m), 516(s), 445(m), 425(s), 410(m), 370(vw), 329(s), 310(m).

$(C_6F_5)_3PCl_2$. 1645(s), 1590(w), 1522(vs), 1495(vs), 1398(s), 1302(s), 1150(m), 1105(vs), 1030(m,br), 990(vs), 840(vw), 828(vw), 765(m), 752(m), 729(m), 720(vw), 675(w), 660(w), 643(m), 632(m), 594(m), 535(s), 465(s), 448(m), 440(m), 420(w), 370(vw), 362(s), 342(s), 310(w).

$(C_6F_5)_3As$. 1650(s), 1590(w), 1555(vw), 1520(vs), 1486(vs), 1390(vs), 1290(s), 1260(vw), 1142(m), 1090(vs), 1050(w), 1030(m), 980(vs), 820(m), 805(s), 760(vw), 755(m), 728(m), 690(w), 625(m), 585(m), 490(m-s), 442(m), 380(m,br), 370(w), 295(s), 275(w).

$(C_6F_5)_3AsCl_2$. 1644(s), 1590(w), 1520(vs), 1490(vs), 1390(s), 1335(m), 1290(m), 1280(m), 1150(w), 1110(s), 1090(vs), 1025(m), 1005(s), 980(vs), 822(m-s), 755(m), 745(w), 715(m), 620(m), 492(m), 442(m), 390(m), 370(w), 295(s), 272(w).

$(C_6F_5)_3AsO$. 1650(s), 1595(w), 1520(vs), 1490(vs), 1465(m), 1390(vs), 1289(s), 1280(s), 1245(vw), 1150(m), 1115(s), 1086(vs), 1045(m), 1020(m), 1010(m), 980(vs), 928(vs), 820(s), 755(m), 745(w), 720(m), 625(m), 585(w), 492(m), 442(m), 390(m), 370

The pentafluorophenyl group absorbs in several different regions; the absorptions at ca. 1650, 1522, 1485, 1268 and 586 $cm.^{-1}$ are due to ω (C-C), and those at about 1392, 1296, 1150, 1100, 980, 730, 640, and 370 $cm.^{-1}$ may be assigned to ν(CF). A single band at 445 $\pm$ 3 (m) is attributed to δ-ring (in-plane), and two bands 730 $\pm$ 5 (m) and 310 $\pm$ 2 $cm.^{-1}$ to δ(CF). The characteristic doublet at ca. 1500 $cm.^{-1}$ and the strong band at ca. 1640 $cm.^{-1}$ are very helpful for identification purposes.

A comparison of the spectra of the phosphorus and arsenic analogues shows that all vibrations appear at about the same place with the exception of the phenyl-element vibrational modes, which appears at 849 $cm.^{-1}$ in $(C_6F_5)_3P$ and falls to 805 $cm.^{-1}$ in $(C_6F_5)_3As$; this is understandable in terms of the increase in the mass of the central atom. Two bands, at 425(s) and 329(s)$cm.^{-1}$, in the spectrum of $(C_6F_5)_3P$ have been assigned to the asymmetric and symmetric stretch of the PC_3 unit,[98] these are probably moved to higher positions, 465(s) and 342(s)$cm.^{-1}$, in the spectrum of $(C_6F_5)_3PCl_2$.

A strong absorption at 362 $cm.^{-1}$ in $(C_6F_5)_3PCl_2$ has been assigned to Cl-P-Cl asymmetric stretch.[93] A strong, sharp absorption at 928 $cm.^{-1}$ in $(C_6F_5)_3AsO$ is assigned to the As-O stretching vibration and, as would be expected, this absorption occurs at a higher frequency than that of $(C_6H_5)_3AsO$ (881 $cm.^{-1}$).[83]

(3) Halogen adducts of $(Me_2N)_3M$.

(a) $(Me_2N)_3P$-Hal_2 adducts.

In general, the infrared spectra of the aminophosphine adducts [$(Me_2N)_3P\ Hal_2$, $(Me_2N)_3PI_nBr_{4-n}$ and $(Me_2N)_3PI_nCl_{4-n}$] prepared during this study were very similar in the position and intensity of the bands and showed many absorptions which may be readily assigned from general infrared data. A summary of spectral bands for some of the adducts is given in Table 22.

Table 22. Infrared Spectra of $(Me_2N)_3P\text{-}Hal_2$ adducts

$(Me_2N)_3PClI$. 2930(s), 2890(s), 2812(m), 1480(s), 1455(s), 1410(s), 1370(m), 1310(vs), 1175(vs), 1160(sh), 1075(s), 1000(br,vs), 765(s), 720(vw), 660(sh), 650(s), 525(s), 445(s), 315(br,m).

$(Me_2N)_3PBrI$. 2930(s), 2885(s), 2818(m), 1480(s), 1455(s), 1410(s), 1370(m), 1315(vs), 1175(vs), 1160(s), 1150(sh), 1072(s), 1005(br,vs), 765(s), 645(s), 515(sh), 495(s), 440(m), 290(br,m).

$(Me_2N)_3PBrI_2$. 2925(s), 2880(s), 2815(m), 1470(s), 1455(s), 1410(s), 1370(m), 1310(vs), 1200(vw), 1170(vs), 1150(s), 1145(sh), 1100(vw), 1065(s), 1000(br,vs), 760(s), 720(vw), 640(s), 512(sh), 475(s), 440(m), 290(br,m).

$(Me_2N)_3PCl_3I$. 2925(s), 2890(s), 2812(m), 1480(s), 1450(s), 1410(s), 1370(m), 1315(vs), 1220(vw), 1175(vs), 1160(s), 1150(s), 1105(vw), 1075(vs), 1000(br,vs), 770(s), 720(w), 660(sh), 650(s), 520(s), 450(s), 310(br,m).

$(Me_2N)_3PI_4$. 2930(s), 2880(s), 2815(m), 1470(s), 1450(s), 1410(s), 1370(m), 1300(vs), 1200(vw), 1170(vs), 1150(s), 1140(sh), 1100(vw), 1060(s), 998(br,vs), 755(s), 720(vw), 675(vw), 640(s), 475(s), 425(vw), 280(br,m).

In the region 2940-2800 $cm.^{-1}$, there are three C-H stretching vibrations (ca. 2930, 2890, 2810 $cm.^{-1}$), the band at ca. 2810 $cm.^{-1}$ was of great diagnostic value and has been discussed in an earlier section (Part III). CH_3 deformation modes can be readily identified in the region 1490-1410 $cm.^{-1}$. The strong band at about 1300 $cm.^{-1}$ probably results from $P\text{-}N(CH_3)_2$ vibration[122] as do the strong absorptions in the region 1010-990 $cm.^{-1}$.[123,124] The strong band at about 1170 $cm.^{-1}$ may be assigned to the asymmetric NC_2-stretching vibrations, the corresponding

absorption in $(Me_2N)_3P$ occurring at the slightly low frequency of 1155 $cm.^{-1}$ [125] The chlorine-containing adducts showed a shoulder (m-s) at 660 $cm.^{-1}$ which was not observed in the bromo or iodo compounds; this is assigned to the P-Cl stretching vibration. The bromo compounds showed an absorption at about 510 $cm.^{-1}$ (absent in chloro or iodo compounds) which may be attributed to the P-Br stretch. As would be expected, both P-Cl and P-Br vibrations lie at the extreme upper limit of the frequencies generally assigned to these bonds.[120]

(b) $(Me_2N)_3As\text{-}Hal_2$ adducts.

The infrared spectra of the compounds prepared from the $(Me_2N)_3As/Hal_2$ reactions are summarised in Table (23).

Table (23). Infrarod Spectra of $(Me_2N)_3As\text{-}Hal_2$ adducts.

$(Me_2N)_3AsBr_2$. 2960(m), 2850(s), 2802(m), 1580(vw), 1470(s), 1450(s), 1412(m), 1255(s), 1155(vs), 1050(s), 1020(w), 930(br,vs), 720(w).

$(Me_2N)_3AsBr_4$. 2960(m), 2850(s), 2806(m), 1580(vw), 1480(s), 1450(s), 1415(m), 1260(s), 1155(vs), 1110(w), 1055(s), 1020(w), 930(br,vs), 720(w), 680(w).

$[(Me_2N)_4As]I_2Br$. 2955(m), 2848(s), 2800(m), 1470(s), 1450(s), 1415(m), 1265(s), 1155(s), 1110(vw). 1060(s), 1010(w), 930(br,vs), 820(vw), 720(w), 615(vs), 485(w), 395(m), 340(m).

Table (23) cont. Infrared Spectra of $(Me_2N)_3As\text{-}Hal_2$ adducts

$[(Me_2N)_4As]I_2Cl$. 2955(m), 2850(s), 2802(m), 1470(s), 1450(s), 1412(m), 1260(s), 1155(s), 1105(vw), 1060(s), 930(br,vs), 615(vs), 485(m), 395(m), 340(br,m).

$[(Me_2N)_4As]ICl_2$. 2960(s), 2850(s), 2805(m), 1480(m), 1450(s), 1415(m), 1260(s), 1160(vs), 1105(vw), 1060(s), 1020(w), 930(br,vs), 615(vs), 485(br,m), 395(m).

$[(Me_2N)_4As]Cl$. 2960(s), 2850(s), 2810(m), 1480(m), 1450(s), 1415(m), 1260(s), 1160(vs), 1110(w), 1060(s), 1022(vw), 930(br,vs), 615(s), 485(m), 395(m).

EXPERIMENTAL

E X P E R I M E N T A L

E X P E R I M E N T A L

I General Techniques:

(1) Handling of Materials:-

Most of the compounds studied in this work were extremely moisture sensitive, strict precautions were required to ensure absence of moisture and air at all stages in their study. This was achieved by the extensive use of a nitrogen-filled dry box containing phosphorus pentoxide. The nitrogen was commercial oxygen free nitrogen dried by passage through a column of molecular sieve (AEI - Birlec Ltd., absorber type AB 12.5).

(2) Vacuum System:-

The other method of handling the compounds involved the use of a vacuum system, which was made up of a pumping unit connected *via* protective sludge traps to a main line from which branched various sub-sections designed for special operations - Vapour pressure measurement, Conductometric titrations using chlorine, Freeze-drying.

Vapour Pressure Measurement:-

For the vapour pressure study of the system $(C_6F_5)_3P\text{-}Br_2$ a special all glass system was made (Fig. 15). The spiral gauge (F) in this system was used as a null instrument in which the deflection of the pointer was magnified by the optical lever principle. The pointer of the gauge was made to actuate a small delicately balanced mirror which reflected a parallel beam of light on to a scale situated at a distance of 1 meter. The zero point of the instrument on the scale was adjusted.

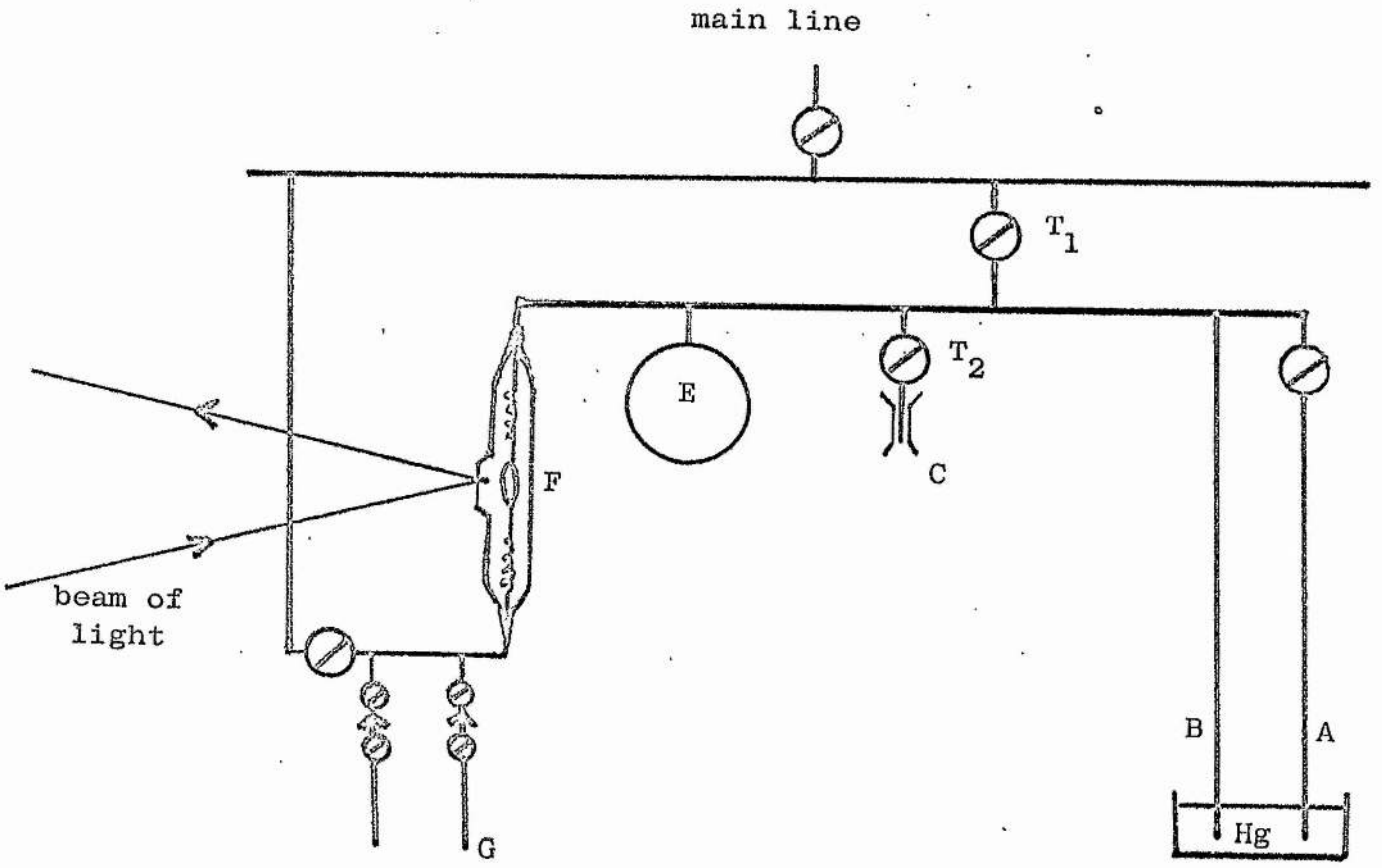


Fig. 15. Vacuum System for Vapour Pressure Study

The compound being investigated was kept in tube (G) and its vapour pressure was compensated by admitting dry air through the capillary leak (C) and the air surge chamber (E). When it was necessary to reduce the pressure in this part of the apparatus, the section was connected to the vacuum line via tap (T_1). Thus when the pressures on either side of the diaphragm had been equilibrated, the pressure could be obtained as a difference in mercury levels between manometers (A) and (B) which were arranged close to one another and which used a common mercury reservoir. Manometer (A) was employed as an ordinary barometer. A cathetometer was used to obtain accurate measurements.

Conductometric Titrations using chlorine:-

These were carried out in a specially designed vacuum system. The dry chlorine was condensed into the trap A of the fractionation line of the system (Fig. 16) and cooled to -78°C (acetone-Drikold mixture) and then pumped off to remove the more volatile impurities. It was then fractionally distilled into trap B by closing the tap (T_3) and cooling the trap B to -183°C (liquid air). When the distillation was complete the tap (T_2) was closed and the chlorine was again fractionally distilled into trap C, by warming the trap B and cooling the trap C to -78°C. The dry chlorine was stored in trap C for use in conductometric titrations. The trap C of the fractionation line was attached to a tube of known capacity (D) between taps (T_5) and (T_6). The tube (D) was calibrated by opening tap (T_5) and keeping tap (T_6) closed and allowing chlorine vapours

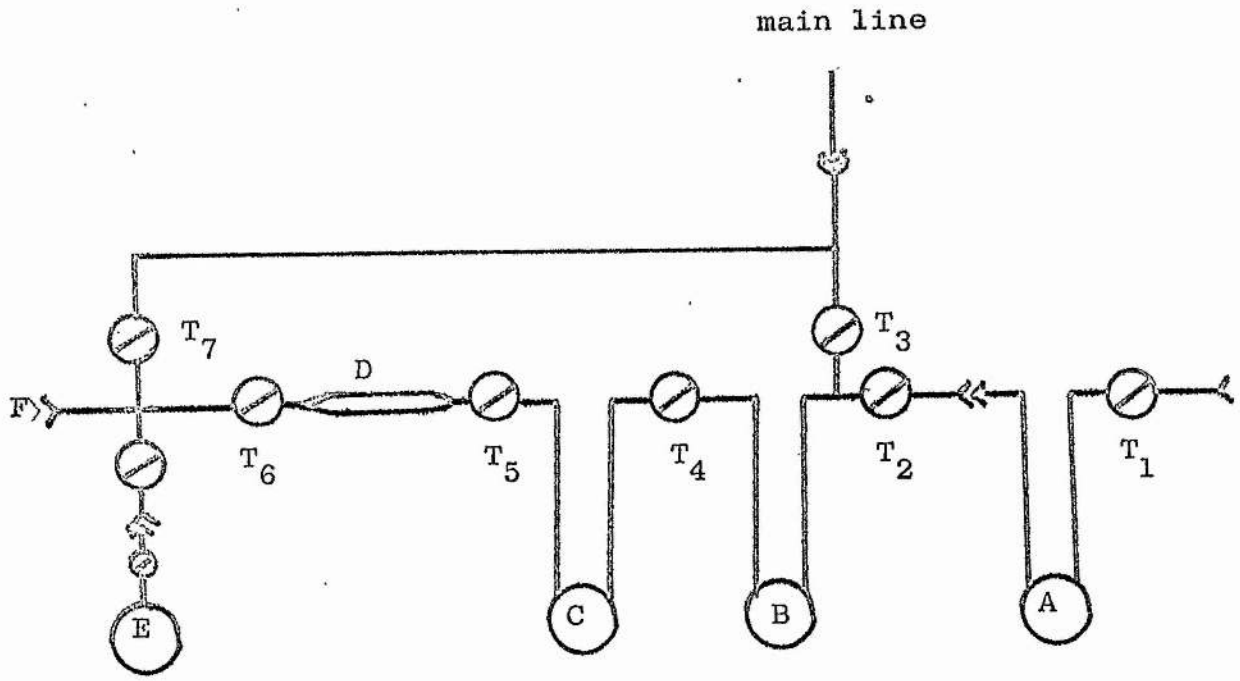


Fig. 16. Vacuum System for Conductometric Titrations using chlorine

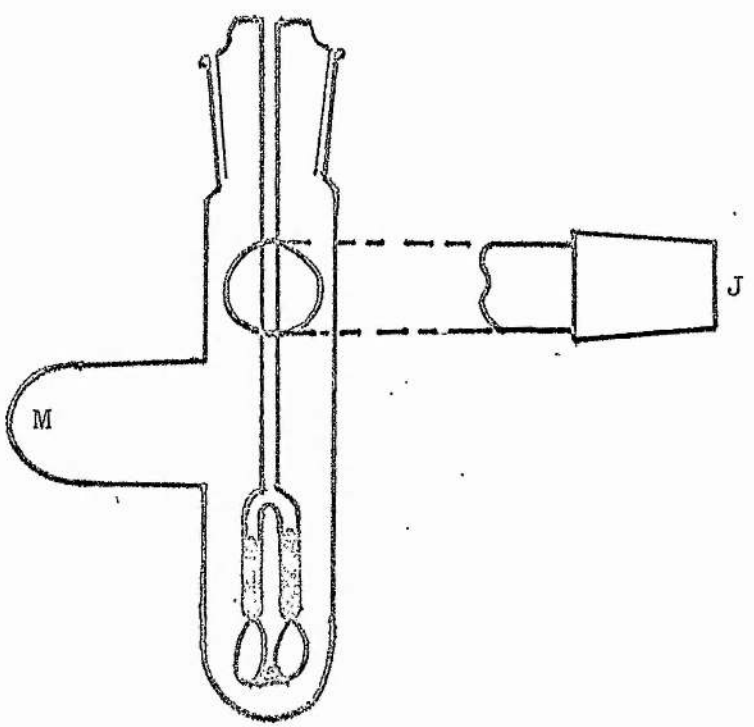


Fig. 17. Conductance Cell

from trap C at -78°C to fill the tube. Then tap (T_5) was closed and the chlorine in the tube (D) was distilled into a light bulb (E) and weighed. The process was repeated several times for consistent results. The average weight of chlorine for the volume between taps (T_5) and (T_6) was worked out.

The conductance cell was attached to the far end (F) of the vacuum system. It was modified to facilitate the distillation of small amounts of chlorine into the cell (Fig.17). The methyl cyanide solution of the compound was frozen in the cold finger (M), and known weights of chlorine from the tube (D) distilled in, and on melting and forming a solution, rotation of the cell about the joint (J) brought the solution into contact with the electrodes. Successive additions of chlorine were made from the calibrated tube (D), and when solution was complete the resistance was measured repeatedly until constant.

(3) Conductance Measurements:-

Conductance measurements were made at 25°C in a sealed cell. A standard pair of smooth dipping electrodes (cell constant 0.330cm^{-1}) was used. A weighed amount of dry solvent was placed in the cell and transferred to the dry box where successive additions of the solid (ca. 0.02 m.mole lots) were made from small sample tubes. After each addition when the solution was complete the cell was placed in a thermostat bath at 25°C and the resistance was measured using a Phillips PR9500 resistance bridge operating on 1000 c/s current. Molar conductances

were calculated and plotted against $\sqrt{c}m$. The concentration 0.01M was chosen as standard for comparison.

(4) Conductometric Titrations:-

A convenient technique for studying the reactions of R_3M compounds with halogens has been shown to be conductometric titration [25,26]. The apparatus used was designed so that the titration could be carried out on a small scale without the solutions' coming into contact with tap grease or atmospheric moisture. A description of the apparatus and its operation has been published [56]. The concentrations of the solutions used were carefully prearranged so that the desired range of mole ratio would be covered. Methyl cyanide was usually employed as a solvent because of its high dielectric constant (36.7 at 25°C). Nitrobenzene was also used occasionally.

The dipping electrodes and the resistance bridge used were the same ones previously mentioned for conductometric measurements. The conductance was measured when equilibrium had been attained after each addition of halogen solution.

(5) Cryoscopy:-

The apparatus was an all glass one with Quick Fit joints and a side arm for the introduction of the solute. Nitrobenzene was used as a solvent. A water-ice mixture at 0.5°C was the cooling agent. After the freezing point of the solvent had been found, a known amount of the sample was introduced and the freezing point redetermined. The molecular weight of the substance was calculated from the depression in freezing points. (Cryoscopic constant of nitrobenzene = 71°C per mole per 100 g. [57]).

(6) Infrared spectra:-

Infrared spectroscopy was extensively used throughout this work for direct determination of purity and identification of the compounds.

IR spectra in the range 625-4000 cm^{-1} were recorded on a Perkin-Elmer Model 237 grating spectrophotometer, and spectra in the 200-4000 cm^{-1} range on a Perkin-Elmer Model 621 grating spectrophotometer. A Perkin-Elmer Model 137 infracord fitted with sodium chloride optics was also used. The samples were generally prepared in drybox as mulls in nujol, hexachlorobutadiene, or KelF no. 3 fluorocarbon oil, and then placed between plates of sodium chloride or caesium iodide, protected when necessary by polythene sheet. Solutions were made up in dry chloroform or methyl cyanide and contained in a 0.2 mm. path length cell with silver chloride windows.

(7) Ultraviolet spectra:-

Ultraviolet spectra were recorded on a Unicam SP800 UV/visible recording spectrophotometer. Stoppered quartz cells of 1 cm., 0.5 cm., or 0.1 cm. path lengths were used. The measurements were made at room temperature (ca. 18°C).

(8) Analyses:-

Microanalyses for carbon, hydrogen, nitrogen and arsenic ~~analyses~~ were carried out by A. Bernhardt, Max-Planck Institut, Mülheim, Germany.

Halogen was determined by Volhard's method after preliminary treatment of the compounds. Before analyses the solids were hydrolysed with excess of 2M sodium hydroxide. This was usually done in a closed system to prevent the possible escape of hydrogen halide. The solution

was allowed to stand for 2 hours and then boiled to ensure complete hydrolysis, cooled, acidified with sulphuric acid, and then treated with sulphur dioxide to reduce any hyponalite ion present. Excess of sulphur dioxide was removed by boiling and the solution was cooled and neutralised with ammonium hydroxide solution. Halide ion was then estimated by Volhard's method.

In the case of compounds containing mixed halogen (chlorine, bromine and iodine), the total halogen content was determined as above. To determine chlorine, bromine and iodine individually a modification of Jannasch's method [58] of selective oxidation was used. 25 ml. of the solution was treated with 3 ml. glacial acetic acid and 5 ml. 20 volume hydrogen peroxide. The selectively oxidised iodine was steam distilled in an all-glass apparatus into ammonical hydrazine solution and the resultant iodide ion determined by Volhard's method. The residual solution containing bromide and chloride, was neutralised with ammonium hydroxide solution, acidified with sulphuric acid, then treated with hydrogen peroxide. The liberated bromine was distilled into ammonical hydrazine as before and the bromide ion estimated in the usual way. The residual solution containing chloride was neutralised with concentrated ammonia and chloride determined.

During the later part of the research a more convenient method was found to be that of potentiometric titration [59]. Potentiometrically a mixture or halides can be readily analysed by a single titration with silver nitrate in the presence of a silver electrode. In a typical

experiment 20 ml. of the hydrolysed solution was pipetted into a 150 ml. beaker, acidified with 5 ml. freshly boiled 6N nitric acid and 50 ml. of water added. A silver wire was used as an indicator electrode and a glass electrode as a reference electrode. Electrodes were placed in the halide solution and the solution was kept stirring during the titration using a magnetic stirrer. The electrode potential (mV) of the initial solution was determined, and the measuremont was repeated at intervals of 0.1 ml. addition of 0.1N silver nitrate from the burette. When the potential changed somewhat more rapidly as the end point was approached, the potential readings were taken at more frequent intervals, and eventually after each drop. A graph was plotted of mV readings versus ml. of silver nitrate solution used. The point of inflections were regarded as the end point of the titration.

Mercury:-

Mercury in compounds was reduced to the metallic state by mono-ethanolamine [60] and weighed as such. About 0.1 g. of the sample was refluxed with ethanolamine for five minutes; cooled, and diluted with water. The supernatant liquid was removed and the mercury was collected into a single globule. The globule was washed with water, transferred to a weighed filter crucible, again washed with water, and finally with dry analar acetone. The crucible was then dried on a water pump and the mercury weighed.

II Purification of Materials:

A Solvents:

(1) Methyl cyanide:-

Pure anhydrous methyl cyanide suitable for conductance studies was prepared by a modification of the method described by Smith and Witten [61]. The commercial material (Hopkin and Williams) was allowed to stand over potassium hydroxide pellets for 7 days. It was then filtered and distilled into a flask containing calcium chloride (14-20 mesh), over which it was left standing for a further period of several days. It was then again filtered and distilled on to phosphorus pentoxide. The distillate was refluxed and distilled repeatedly over phosphorus pentoxide until the phosphorus pentoxide in the receiving flask did not remain bound to the flask when the latter was swirled. The dry solvent was stored over the phosphorus pentoxide until required for use. It was then distilled on the vacuum line to remove traces of drying agent. b.p., 81-82°; $K \times 10^{-7}$ ohm^{-1} cm^{-1} at 25°.

(2) Nitrobenzene:-

Analar grade nitrobenzene was distilled twice, once at atmospheric pressure, when the fraction boiling at 207-208° was collected, and the other at reduced pressure (65-66°, ca. 0.2 mm.). The specific conductance of this nitrobenzene was less than 10^{-7} ohm^{-1} cm^{-1} at 25°.

(3) Carbon Tetrachloride:-

The method used to obtain pure carbon tetrachloride was a variation of that described by Popov and Schmorr [62]. The crude solvent (500 cc.)

was refluxed for 10 hours with a saturated solution of potassium permanganate in 2N sodium hydroxide solution (100 cc.). The carbon tetrachloride was then separated and washed several times with water. After a preliminary drying with anhydrous magnesium sulphate, the carbon tetrachloride was filtered and distilled on to phosphorus pentoxide, and then distilled several times on to fresh phosphorus pentoxide. b.p. = 75.5-76.0° (760 mm.)

(4) Diethyl ether:-

Diethyl ether was dried by refluxing it over sodium wire, after preliminary drying over calcium chloride. It was then distilled, refluxed over lithium aluminium hydride (2g/l), distilled again and stored in a dry box.

(5) Chloroform:-

The commercial grade solvent was washed with a large volume of water to remove ethanol. It was dried by passage through a column of alumina; stored over silica gel and distilled before use.

B. Reagents

(1) Chlorine:-

Commercial chlorine was dried by passage through concentrated sulphuric acid and a drying tower packed with phosphorus pentoxide. When used for conductometric titrations it was further purified on the vacuum line.

(2) Bromine:-

Analar bromine was stored over calcium bromide. It was filtered in a small flask attached to the vacuum system and pumped off to remove

the more volatile impurities. The bromine was then cooled to 0°C and distilled in vacuo into ampoules cooled to -85°C. Thus the known weights of bromine were stored in sealed ampoules. The solutions were made by breaking an ampoule under a known weight of solvent.

(3) Iodine:-

Analar grade iodine was resublimed and stored in a desiccator over phosphorus pentoxide.

(4) Iodine Bromide:-

Commercial material (B.D.H.) was resublimed and stored in a stoppered flask in a desiccator. For conductometric titrations it was made in solution by mixing equivalent quantities of iodine and bromine solutions.

(5) Iodine chloride:-

Commercial iodine chloride (B.D.H.) was purified by melting and allowing it to cool slowly until 80% solidified. The supernatant liquid was decanted and the residue resublimed.

(6) Iodine Trichloride:-

Iodine trichloride was prepared by the method of Booth and Morris [63]. Liquid chlorine was collected under anhydrous conditions in a glass tube, cooled in an acetone-drikold bath (ca. 80°). Powdered iodine was added slowly to liquid chlorine which immediately converted to flocculent, orange, iodine trichloride. When the liquid space was filled with the trichloride, the excess chlorine was evaporated into a second container where the process was repeated. The product was stored in a sealed tube.

During the later part of the research analar grade iodine trichloride was used directly without further purification.

III. Preparations of the Starting Materials:

(1) Triphenylarsine:-

Triphenylarsine was prepared by the Wurtz reaction between arsenic trichloride and chlorobenzene [64], and the crude product was recrystallised from 95% ethanol to constant melting point (m.p. 61°).

(2) Triphenylphosphine:-

The commercial triphenylphosphine (B.D.H.) was recrystallised from 95% ethanol until a constant melting point was obtained. m.p. 79°.

(3) Triphenylstibine:-

Triphenylstibine was available which had been prepared by the Grignard reaction of phenylmagnesium bromide and antimony trichloride [65]. It was recrystallised from 40-50 petroleum ether to constant melting point. m.p. 50°.

(4) Tris(pentafluorophenyl)phosphine:-

Tris(pentafluorophenyl)phosphine was prepared by the Grignard reaction of pentafluorophenylmagnesium chloride and phosphorus tribromide [66]. The Grignard reagent, pentafluorophenylmagnesium chloride was prepared in the manner described previously [67]. 82.3 g. (0.406 mole) of pentafluorochlorobenzene and 76.2 g. (0.406 mole) of ethylene dibromide were mixed in anhydrous ether (100 mls.) and added slowly to 19.7 g. (0.812 mole) of magnesium turnings in anhydrous ether (300 ml.).

A cooling bath, ice water, was used to control the reaction.

$$C_6F_5Cl + 2Mg + BrC_2H_4Br = C_6F_5MgCl + C_2H_4\uparrow + MgBr_2$$

On the completion of the reaction a dark brown solution was obtained. This was cooled to about -30° and 35 g. (0.13 mole) of phosphorus tribromide in 50 mls. ether were added dropwise during one hour. After the addition was complete the flask was allowed to warm to room temperature over 2 hours and stirring continued for a further 2 hours. Finally it was refluxed for a short time. The mixture was then cooled to 0°C, ice-water was added, and 3N hydrochloric acid stirred in until the solution was acidic. The ether phase was separated off, dried over magnesium sulphate and concentrated under reduced pressure to give a brown solid, which on sublimation under reduced pressure at 100-110° gave 30 g. of tris(pentafluorophenyl)phosphine. Yield 43%; m.p. 116°; Found C, 40.79; calculated for $C_{18}F_{15}P$: C, 40.60%.

(5) Tris(pentafluorophenyl)arsine:-

This compound was prepared by the reaction of arsenic trichloride with the Grignard reagent, pentafluorophenylmagnesium bromide [68], a method similar to that employed for the preparation of tris(pentafluorophenyl)phosphine. The sublimed product was white needles, m.p. 106°. (Yield 45%). (Found: C, 37.54; calculated for $C_{18}F_{15}As$: C, 37.50%).

(6) Tris(dimethylamino)phosphine:-

Tris(dimethylamino)phosphine was prepared by a modification of the method described by Burg and Slota [69]. An ether solution of phosphorus trichloride was added to an ether solution of dimethylamine during 2 hours at -10 to -15°C. The bulk of the hydrochloride precipitated was filtered out and the filtrate was concentrated on a rotary pump to give 94-95% of the crude phosphine. The product was further purified by fractional distillation under reduced pressure, and stored in sealed tubes. b.p. 32°/0.5 mm.

(7) Tris(dimethylamino)arsine:

Tris(dimethylamino)arsine was prepared by the reaction between dimethylamine and arsenic trichloride [70]. The method used was similar to the one described for the preparation of tris(dimethylamino)phosphino. As this arsine is very unstable and decomposes spontaneously in the atmosphere, giving white fumes and a penetrative smell, considerable care was taken to avoid the ingress of moisture or oxygen in the preparation, isolation and subsequent purification. b.p. 30°/0.2 mm.

PART I

1 - PREPARATION OF TRIPHENYLPHOSPHINE-HALOGEN ADDUCTS

(i) Triphenylphosphorus dichloride.

Dry chlorine gas in a stream of nitrogen was bubbled into a solution of triphenylphosphine in anhydrous petroleum ether until the solvent assumed a pale yellow colour. Cooling was necessary. White crystals of the dichloride precipitated and were filtered off and washed with anhydrous ether. (Found: Cl, 20.9. Calc. for $C_{18}H_{15}PCl_2$: Cl, 21.2%).

(ii) Triphenylphosphorus dibromide.

Bromine (0.641 g., 4.0 m.mole) dissolved in methyl cyanide (10 ml.) was added dropwise to triphenylphosphine (1.05 g., 4.0 m. mole) suspended in methyl cyanide (20 ml.). Solution was complete soon after addition of halogen began and then white crystals precipitated. The crystals were filtered in the dry box and washed with anhydrous ether. (Found: Br, 37.8. Calc. for $C_{18}H_{15}PBr_2$: Br, 37.9%).

(iii) Triphenylphosphorus chloride iodide.

A solution of iodine trichloride (0.82 g., 3.52 m.mole) in methyl cyanide (10 ml.) was added to a suspension of triphenylphosphine (1.85 g., 7.04 m.mole) in methyl cyanide (15 ml.). The triphenylphosphine dissolved and on the addition of anhydrous ether yellow crystals precipitated, m.p. 122-125°. (Found: C, 50.0; H, 3.61; Cl, 8.25; I, 29.3. $C_{18}H_{15}PClI$ requires: C, 50.9; H, 3.53; Cl, 8.34; I, 29.9%).

(iv) Triphenylphosphorus trichloride iodide.

Iodine trichloride (0.51 g., 2.19 m.mole) in methyl cyanide (5 ml.) was added to a solution of triphenylphosphine (0.57 g., 2.19 m.mole) in methyl cyanide (20 ml.). A yellow solution was produced and addition of ether to this solution caused yellow crystals to be precipitated, m.p. 94-95°. (Found: Cl, 21.7; I, 24.81. $C_{18}H_{15}PCl_3I$ requires: Cl, 21.5; I, 25.60%).

(v) Preparation of $[(Ph_3P)_2Cl]I_3$.

Iodine chloride (1.32 g., 8.1 m.mole) in methyl cyanide (10 ml.) was added slowly to triphenylphosphine (2.14 g., 8.1 m.mole) suspended in methyl cyanide (20 ml.). The triphenylphosphine dissolved and the solution became brownish yellow. Yellow crystals were precipitated by the addition of anhydrous ether, m.p. 218° decomp. (Found: C, 45.08; H, 3.21; Cl, 3.8; I, 40.2. $C_{36}H_{30}P_2ClI_3$ requires: C, 45.96; H, 3.19; Cl, 3.80; I, 40.50%).

(vi) Preparation of $[(Ph_3P)_2Br]HgBr_3$.

Mercury(11)bromide (1.89 g., 5.0 m.mole) dissolved in hot ethyl alochol was added to triphenylphosphine (2.62 g., 10.0 m.mole) in hot ethyl alcohol. White crystals of $[(Ph_3P)_2HgBr_2]$ were precipitated, filtered off, and dried under a vacuum.

A solution of bromine (0.69 g., 4.3 m.mole) in methyl cyanide (10 ml.) was added to $[(Ph_3P)_2HgBr_2]$ (3.8 g., 4.3 m.mole) suspended in methyl cyanide (25 ml.). The resulting solution was colourless and white crystals were precipitated by the addition of anhydrous ether, m.p. 130°. (Found: C, 41.64; H, 3.12; Hg, 19.02; Br, 29.6. $C_{36}H_{30}P_2HgBr_4$ requires C, 41.45; H, 2.90; Hg, 19.2; Br, 30.59%).

(vii) Attempted preparation of $[(Ph_3P)_2Cl]HgCl_3$.

(a) Mercury(11) chloride (0.9 g., 3.32 m.mole) dissolved in methyl cyanide (20 ml.) was added to a methyl cyanide solution of triphenylphosphorus dichloride (1.11 g., 3.32 m.mole) containing triphenylphosphine (0.87 g., 3.32 m.mole). Anhydrous ether (50 ml.) was added to this solution until white crystals precipitated. These were filtered off and dried. (Found: Hg, 31.9; Cl, 22.8. $C_{18}H_{15}PHgCl_4$ requires: Hg, 33.2; Cl, 23.5%). That is, the compound isolated is $[Ph_3PCl]HgCl_3$.

(b) An alternative route to this compound was thought to be the addition of chlorine to $[(Ph_3P)_2HgCl_2]$.

A stream of dry chlorine in nitrogen was bubbled into a solution of $[(Ph_3P)_2HgCl_2]$ in chloroform until the solvent assumed a pale yellow colour. On the addition of anhydrous ether white cyrstals were precipitated. These were filtered off and identified by analysis as $[Ph_3PCl]HgCl_3$.

(viii) Isolation of triphenylphosphorus di-iodide at 0.5:1 ($ICl:Ph_3P$) mole ratio.

Iodine chloride (0.317 g., 1.95 m.mole) dissolved in methyl cyanide (10 ml.) was added to a solution of triphenylphosphine (1.02 g., 3.90 m.mole) in methyl cyanide (25 ml.). A yellow solution was formed and after a few moments yellow crystals were precipitated. These were filtered off, washed with ether, and dried under vacuo, m.p. 175-179°. (Found: C, 41.76; H, 2.81; I, 49.0. $C_{18}H_{15}PI_2$ requires: C, 42.24; H, 2.90; I, 49.2%).

2 - PREPARATION OF TRIPHENYLARSINE-HALOGEN ADDUCTS.

(i) Triphenylarsenic dichloride.

A stream of dry chlorine in nitrogen was bubbled into a solution of triphenylarsine in dry carbon tetrachloride until the solvent assumed a pale yellow colour. White crystals of the dichloride precipitated and were filtered under nitrogen, washed with anhydrous ether, and dried in vacuo, m.p. 204-205°. (Found: Cl, 19.05. $C_{18}H_{15}AsCl_2$ requires: Cl, 18.80%).

(ii) Triphenylarsenic dibromide.

A solution of bromine (0.590 g., 3.7 m.mole) in methyl cyanide (10 ml.) was added to a solution of triphenylarsine (1.13 g., 3.7 m.mole) in methyl cyanide (20 ml.). The resulting solution was colourless and white crystals were precipitated. These were filtered off, washed with ether, and dried in vacuo, m.p. 215°. (Found: Br, 34.2. $C_{18}H_{15}AsBr_2$ requires: Br, 34.3%).

(iii) Triphenylarsenic trichloride iodide.

(a) Iodine chloride (1.05 g., 6.5 m.mole) in methyl cyanide (10 ml.) was added dropwise to a solution of triphenylarsenic dichloride (2.45 g., 6.5 m.mole) in methyl cyanide (20 ml.). The resulting yellow solution was freeze dried to a yellow oil, which on trituration with anhydrous ether gave a bright yellow solid, m.p. 80-81°. (Found: C, 40.23; H, 2.88; As, 13.78; Cl, 19.59; I, 23.35. $C_{18}H_{15}AsCl_3I$ requires: C, 40.2; H, 2.78; As, 13.89; Cl, 19.80; I, 23.60%).

(b) An alternative route to this compound is the addition of iodine trichloride (x mole) in methyl cyanide to triphenylarsine (x mole) in the same solvent. The compound may be isolated either by freeze drying or by ether precipitation.

(iv) Triphenylarsenic chloride dibromide iodide.

(a) Iodine chloride (.502 g., 3.1 m.mole) dissolved in methyl cyanide (10 ml.), was added to triphenylarsenic dibromide (1.45 g., 3.1 m. mole) suspended in methyl cyanide (20 ml.). A red solution was produced and addition of ether to this and cooling to 0° yielded red crystals, m.p. 92-94°. (Found: C, 35.4; H, 2.58; Cl, 5.60; Br, 26.0; I, 19.7. $C_{18}H_{15}AsClBr_2I$ requires: C, 34.4; H, 2.40; Cl, 5.64; Br, 25.43; I, 20.19%).

(b) Addition of ether to a methyl cyanide solution of iodine trichloride (0.677 g., 2.9 m.mole) and triphenylarsenic dibromide (1.35 g., 2.9 m.mole) precipitated red needles, which were filtered off and washed with ether, m.p. 93°. (Found: C, 34.88; H, 2.71; Cl, 5.67; Br, 25.80; I, 19.50%).

(v) Triphenylarsenic pentachloride iodide.

Iodine trichloride (0.572 g., 2.45 m.mole) in methyl cyanide (10 ml.) was added to triphenylarsenic dichloride (0.92 g., 2.45 m.mole) dissolved in methyl cyanide (20 ml.) The resulting solution was bright yellow and on addition of ether (25 ml.) gave yellow crystals, m.p. 122-124°. (Found: C, 35.28; H, 2.45; As, 12.01; Cl, 28.1; I, 19.9. $C_{18}H_{15}AsCl_5I$ requires: 35.40; H, 2.40; As, 12.30; Cl, 29.1; I, 20.8%).

(vi) Hydroxytriphenylarsonium dichloroiodate (1) chloride.

Iodine chloride (0.49 g., 3.05 m.mole) in moist methyl cyanide (10 ml.) was added to triphenylarsenic dichloride (1.15 g., 3.05 m.mole) dissolved in moist methyl cyanide (15 ml.). The yellow solution was freeze dried, and the resultant yellow solid shaken with ether, filtered and dried, m.p. 83-84°. (Found: C, 49.26; H, 3.44; As, 17.22; Cl, 12.24; I, 14.4%. $C_{36}H_{30}As_2O_2ICl_3$ requires: C, 49.12; H, 3.64; As, 17.10; Cl, 12.12; I, 14.44%).

3 - PREPARATION OF TRIPHENYLSTIBINE-HALOGEN ADDUCTS.

(i) Triphenylantimony dichloride.

Dry chlorine gas was bubbled into a solution of triphenylstibine in chloroform until a strong green colour showed the presence of excess chlorine. White crystals of the dichloride separated. These were filtered off, washed with chloroform, and dried in vacuo, m.p. 143°. (Found: Cl, 16.4. $C_{18}H_{15}SbCl_2$ requires: Cl, 16.6%).

(ii) Triphenylantimony chloride iodide.

(a) Iodine chloride (0.52 g., 3.22 m.mole) in methyl cyanide (5 ml.) was added to triphenylstibine (1.14 g., 3.22 m.mole) suspended in methyl cyanide (10 ml.). The triphenylstibine dissolved and the resulting solution was pale yellow. By cooling this to 0° white crystals were precipitated, m.p. 159-161°. (Found: C, 41.6; H, 2.94; Cl, 6.1; I, 25.4. $C_{18}H_{15}SbClI$ requires: C, 41.8; H, 2.90; Cl, 6.9; I, 24.5%).

(b) Iodine trichloride (0.314 g., 1.35 m.mole) dissolved in methyl cyanide (10 ml.) was added to a solution of triphenylstibine

(0.955 g., 2.70 m.mole) in methyl cyanide (20 ml.). White crystals of Ph_3SbClI precipitated; these were filtered off and dried in vacuo, m.p. 159-160°. (Found: Cl, 6.53; I, 23.8%).

(iii) Triphenylantimony dichloride from conductometric titrations.

(a) A solution of iodine chloride (0.343 g., 2.12 m.mole) in methyl cyanide (5 ml.) was added to a solution of triphenylstibine (0.374 g., 1.06 m.mole) in methyl cyanide (20 ml.). White crystals precipitated on partial evaporation of the solvent were filtered off and dried under vacuum, m.p. 143-144°. (Found: Cl, 16.8. $C_{18}H_{15}SbCl_2$ requires: Cl, 16.6%).

(b) Iodine trichloride (0.238 g., 1.02 m.mole) dissolved in methyl cyanide (10 ml.) was added to triphenylstibine (0.36 g., 1.02 m.mole) in methyl cyanide (15 ml.) The dark red solution was concentrated by partial evaporation of the solvent to give white crystals, which were filtered off and identified by m.p. and analysis, m.p. 142-144°. (Found: Cl, 17.12%).

(iv) Oxy bis(triphenylantimony) di-iodide.

Iodine (0.33 g., 1.3 m.mole) dissolved in methyl cyanide (20 ml.) was added to triphenylantimony chloride iodide (0.63 g., 1.3 m.mole) in methyl cyanide (20 ml.). A red solution was produced; addition of ether to this and cooling to 0° yielded red crystals, m.p. 195-198°. (Found: C, 44.53; H, 3.04; I, 25.7. $C_{36}H_{30}Sb_2OI_2$ requires: C, 44.4; H, 3.08; I, 26.0%).

PART II

A - PREPARATION OF TRIS(PENTAFLUOROPHENYL)PHOSPHINE-HALOGEN ADDUCTS.

(1) Tris(pentafluorophenyl)phosphorus dichloride.

(a) Chlorine was bubbled through a solution of Tris(pentafluorophenyl) phosphine (1.0 g., 1.88 m.mole) in methyl cyanide, until sudden crystallisation took place. The white crystals were filtered off in a dry box, washed with methyl cyanide and dried in vacuo, m.p. 229-232°. Yield = 0.92 g., 80%. (Found: C, 36.02; Cl, 11.95. $C_{18}F_{15}PCl_2$ requires: C, 35.9; Cl, 11.8%).

(b) Iodine chloride (0.61 g., 3.76 m.mole) dissolved in methyl cyanide (10 ml.) was added to a solution of $(C_6F_5)_3P$ (1.0 g., 1.88 m.mole) in the same solvent. The deep red solution was freeze dried and the dark solid residue was sublimed at 160-170°/0.2 mm. to give white crystals, m.p. 230-232°. (Found: Cl, 10.89%).

(c) A solution of iodine trichloride (0.44 g., 1.88 m.mole) in methyl cyanide (10 ml.) was added to a well stirred solution of $(C_6F_5)_3P$ (1.0 g., 1.88 m.mole) in methyl cyanide. The deep red solution when freeze dried gave a dark solid residue, this on sublimation under reduced pressure gave white needles, m.p. 230-232°. (Found: Cl, 12.05%).

(2) Tris(pentafluorophenyl)phosphorus tetrabromide.

Bromine (0.94 g., 5.86 m.mole) dissolved in methyl cyanide (10 ml.) was added to tris(pentafluorophenyl)phosphine (1.56 g., 2.93 m.mole) suspended in methyl cyanide (20 ml.). The phosphine dissolved and the resulting solution was brownish yellow. Orange crystals precipitated on the addition of ether were filtered off and washed with ether, m.p. 163-165°.

(Found: Br, 37.17%. Calculated for $C_{18}F_{15}PBr_4$: Br, 37.52%).

(3) Tris(pentafluorophenyl)phosphorus dibromide di-iodide.

Tris(pentafluorophenyl)phosphine (1.22 g., 2.29 m.mole) was dissolved in a solution of iodine bromide (0.95 g., 4.58 m.mole) in methyl cyanide (20 ml). No precipitate appeared on the addition of a large excess of ether (50 ml.) The solution was freeze dried, and the resultant orange red oil shaken with ether. Attempts to crystallise the oil were not successful. (Found: Br, 16.16; I, 26.90. $C_{18}F_{15}PBr_2I_2$ requires: Br, 16.91; I, 26.85%).

(4) Tris(pentafluorophenyl)phosphorus tribromide iodide.

Iodine bromide (0.83 g., 4.0 m.mole) dissolved in methyl cyanide (10 ml.) was added to tris(pentafluorophenyl)phosphine (0.71 g., 1.33 m.mole) in methyl cyanide (20 ml.). The resulting deep red solution gave no precipitate on the addition of a large excess of ether. The solution, when freeze dried, gave a deep red oily residue. This was washed with anhydrous ether to remove excess iodine. (Found: Br, 26.05; I, 14.65. $C_{18}F_{15}PBr_3I$ requires: Br, 26.69; I, 14.13%).

B - TRIS(PENTAFLUOROPHENYL)ARSINE-HALOGEN ADDUCTS.

(1) Tris(pentafluorophenyl)arsenic dichloride.

(a) Dry chlorine was bubbled into a solution of tris(pentafluorophenyl)arsine (1.0 g., 1.74 m.mole) in methyl cyanide until the solvent assumed a yellow colour. White crystals of the dichloride

precipitated and were filtered off, washed with methyl cyanide and dried in vacuo, m.p. 214-216°. Yield = 0.86 g., 78%. (Found: C, 34.3; Cl, 10.9. $C_{18}F_{15}AsCl_2$ requires: C, 33.4; Cl, 11.0%).

(b) Iodine chloride (0.29 g., 1.8 m.mole) in methyl cyanide (5 ml.) was added to $(C_6F_5)_3As$ (0.52 g., 0.9 m.mole) dissolved in methyl cyanide (20 ml.). The resulting solution was deep red, and on freeze drying gave a dark solid residue. This was washed with methyl cyanide to remove iodine and the white crystals identified by m.p. and analysis, m.p. 210-215°. (Found: Cl, 11.2%).

(c) A solution of iodine trichloride (0.237 g., 1.01 m.mole) in methyl cyanide (10 ml.) was added to a solution of $(C_6F_5)_3As$ (0.58 g., 1.01 m.mole) in methyl cyanide (20 ml.). A red solution was produced and when cooled to 0° the solution deposited white crystals. These were filtered off, washed with methyl cyanide and dried in vacuo, m.p. 215-216°. (Found: Cl, 10.85%).

(2) Tris(pentafluorophenyl)arsine oxide.

Water (1 ml.) was added to a solution of tris-(pentafluorophenyl) arsenic dichloride (0.5 g.) in boiling ethyl alcohol (20 ml.). White crystals were precipitated on cooling to 0°. These were re-crystallised from 95% ethyl alcohol, m.p. 198-199°. (Found: C, 36.5. $C_{18}F_{15}AsO$ requires: C, 36.6%).

PART III

A - TRIS(DIMETHYLAMINO)PHOSPHINE-HALOGEN ADDUCTS.

(1) TRIS(DIMETHYLAMINO)PHOSPHORUS DIHALIDES.

(a) Tris(dimethylamino)phosphorus dichloride.

Dry chlorine gas in a stream of nitrogen was bubbled into a solution of tris(dimethylamino)phosphine, [TDP], in anhydrous petroleum ether at -80°. Pale yellow crystals precipitated, were filtered in a dry box, washed with petroleum ether and pumped for several hours on a vacuum line until the yellow tinge completely disappeared, m.p. 266-270°. (decomp). (Found: Cl, 30.12. $C_6H_{18}N_3PCl_2$ requires: Cl, 30.29%).

(b) Tris(dimethylamino)phosphorus dibromide.

Bromine (0.849 g., 5.3 m.mole) dissolved in methyl cyanide (15 ml.) was added dropwise to a solution of TDP (0.86 g., 5.3 m.mole) in methyl cyanide (20 ml.). Heat was evolved, and on addition of anhydrous ether (30 ml.) pale yellow crystals were precipitated. The crystals were filtered off, washed with anhydrous ether and dried in vacuo, m.p. 246-248°. (Found: Br, 49.32. $C_6H_{18}N_3PBr_2$ requires: Br, 49.48%).

(c) Tris(dimethylamino)phosphorus di-iodide.

Iodine (0.97 g., 3.83 m.mole) dissolved in methyl cyanide (25 ml.) was added slowly to a solution of TDP (0.625 g., 3.83 m.mole) in methyl cyanide (10 ml.). Heat was evolved and the resulting solution

was pale yellow. Addition of anhydrous ether (50 ml.) caused the precipitation of yellow crystals which were filtered off, washed with ether and dried in vacuo, m.p. 246-250° (decomp.). (Found: I, 59.95; $C_6H_{18}N_3PI_2$ requires: I, 60.8%).

(d) Tris(dimethylamino)phosphorus bromide iodide.

Iodine bromide (0.768 g., 3.71 m.mole) in methyl cyanide (10 ml.) was added to TDP (0.61 g., 3.71 m.mole) in methyl cyanide (10 ml.). Addition of anhydrous ether to the resulting solution yielded white crystals. These were filtered off, washed with ether and dried in vacuo, m.p. 224-226°. (Found: C, 19.85; H, 4.98; Br, 21.60; I, 34.26. $C_6H_{18}N_3PBrI$ requires: C, 19.5; H, 4.86; Br, 21.59; I, 34.30%).

(e) Tris(dimethylamino)phosphorus chloride iodide.

(i) Iodine chloride (0.76 g., 4.68 m.mole) in methyl cyanide (10 ml.).was added slowly to TDP (0.77 g., 4.68 m.mole) in methyl cyanide (10 ml.) The resulting solution was colourless, and white crystals were precipitated on the addition of anhydrous ether. These were filtered off, washed with ether and dried in vacuo, m.p. 226-235°. (Found: C, 22.36; H, 5.70; Cl, 10.84; I, 39.10. $C_6H_{18}N_3PClI$ requires: C, 22.14; H, 5.57; Cl, 10.89; I, 38.98%).

(ii) Iodine trichloride (0.49 g., 2.1 m.mole) dissolved in methyl cyanide (10 ml.) was added slowly to TDP (0.685 g., 4.2 m.mole) in methyl cyanide (20 ml.). Addition of anhydrous ether to this solution caused white crystals to be precipitated, m.p. 232-236°. (Found: Cl, 10.9; I, 39.2%).

(2) TRIS(DIMETHYLAMINO)PHOSPHORUS TETRAHALIDES.

(a) Tris(dimethylamino)phosphorus tetrachloride.

Dry chlorine gas in a stream of nitrogen was bubbled into a solution of TDP in methyl cyanide at -30° until the solvent assumed a yellow colour. The solution was brought up to room temperature and anhydrous ether added until yellow crystals precipitated. These were filtered off, washed with ether and dried under slightly reduced pressure, m.p. 75-80° (decomp.). (Found: Cl, 45.59. $C_6H_{18}N_3PCl_4$ requires: Cl, 46.5%).

(b) Tetrahalides of the type $(Me_2N)_3PI_nCl_{4-n}$ and $(Me_2N)_3PI_nBr_{4-n}$.

In general, the tetrahalides in the series $(Me_2N)_3PI_nCl_{4-n}$ and $(Me_2N)_3PI_nBr_{4-n}$ were prepared by adding halogen to TDP in methyl cyanide. The tetrahalide was induced to crystallise by the addition of ether. The crystals were filtered off and washed with ether. Melting points and analytical results of all the tetrahalides prepared are listed in the Table (24).

TABLE (24)

Analytical and Melting Point Data of

The Tetrahalides of $(Me_2N)_3Pl_nCl_{4-n}$ and $(Me_2N)_3Pl_nBr_{4-n}$.

Reaction	Compound isolated	Colour	m.p. °C	Found %					Calculated %				
				C	H	Cl	I	Br	C	H	Cl	I	Br
TDP + ICl_3	$TDPCl_3I$	Yellow	103-104	18.2	4.58	26.83	32.0	-	18.18	4.53	26.76	32.1	-
TDP + 2ICl	$TDPCl_2I_2$	Red Yellow	76-78	15.88	4.18	14.79	51.31	-	14.72	3.69	14.53	52.02	-
TDP + ICl + I_2	$TDPClI_3$	Dark Red	104	12.71	3.33	5.93	66.04	-	12.44	3.10	6.12	65.71	-
TDP + $2I_2$	$TDPI_4$	Chocolate	89-90	10.99	2.95	-	75.96	-	10.70	2.68	-	75.70	-
TDP + IBr+ I_2	$TDPI_3Br$	Dark Red	103-104	12.08	3.13	-	60.99	12.65	11.55	2.89	-	61.03	12.80
TDP + 2IBr	$TDPI_2Br_2$	Dark Red	88-89	12.78	3.59	-	42.98	27.70	12.49	3.12	-	43.97	27.70
TDP + 3IBr	$TDPIBr_3$	Red Orange	94-96	13.87	3.35	-	23.41	44.70	13.60	3.40	-	23.98	45.30
TDP + $2Br_2$	$TDPBr_4$	Orange	90-92	15.10	3.90	-	-	66.50	14.90	3.73	-	-	66.26

B - TRIS(DIMETHYLAMINO)ARSINE-HALOGEN ADDUCTS.

(1) TRIS(DIMETHYLAMINO)ARSENIC DIBROMIDE.

Bromine (0.59 g., 3.69 m.mole) in methyl cyanide (10 ml.) was added slowly to tris(dimethylamino)arsine, [TDA], (0.765 g., 3.69 m.mole) in methyl cyanide (20 ml.). Heat was evolved and the solution became yellow. Addition of anhydrous ether (30 ml.) caused the precipitation of pale yellow crystals, which were filtered off, washed with anhydrous ether, and dried in vacuo, m.p. 92--94°. (Found: Br, 42.67; $C_6H_{18}N_3AsBr_2$ requires: Br, 43.6%).

(2) TRIS(DIMETHYLAMINO)ARSENIC TETRABROMIDE.

Bromine (1.345 g., 8.41 m.mole) dissolved in methyl cyanide (10 ml.) was added slowly to TDA (0.87 g., 4.2 m.mole) in methyl cyanide (15 ml.). An orange red solution was produced and addition of ether to this and cooling to 0° yielded orange needles, m.p. 96-102°C. (Found: C, 14.01; H, 3.62; Br, 59.40. $C_6H_{18}N_3AsBr_4$ requires: C, 13.66; H, 3.42; Br, 60.85%).

(3) TETRAKIS(DIMETHYLAMINO)ARSONIUM CHLORO IODO IODATE (1).

Iodine chloride (1.239 g., 7.65 m.mole) in methyl cyanide (15 ml.) was added to TDA (1.59 g., 7.65 m.mole) in methyl cyanide. The resulting solution was deep red and on addition of ether (25 ml.) red crystals were precipitated. These were filtered off, washed with ether and dried under slightly reduced pressure, m.p. 88-92°. (Found: C, 18.0; H, 4.54; Cl, 6.05; I, 46.30. $C_8H_{24}N_4AsClI_2$ requires: C, 17.80; H, 4.45; Cl, 6.50; I, 46.90%).

(4) TETRAKIS(DIMETHYLAMINO)ARSONIUM DICHLOROIODATE (1).

Iodine trichloride (1.349 g., 5.79 m.mole) in methyl cyanide (15 ml.) was added to a solution of TDA (1.2 g., 5.79 m.mole) in methyl cyanide (15 ml.). Heat was produced; the resulting solution was yellow. On the addition of anhydrous ether to this solution yellow crystals were precipitated, m.p. 102-105°. (Found: C, 21.2; H, 5.25; Cl, 16.1; I, 27.9. $C_8H_{24}N_4AsCl_2I$ requires: C, 21.4; H, 5.25; Cl, 15.8; I, 28.2%).

(5) TETRAKIS(DIMETHYLAMINO)ARSONIUM BROMO IODO IODATE (1).

Iodine bromide (1.41 g., 6.8mmole) in methyl cyanide (15 ml.) was added to TDA (1.4 g., 6.8mmole) in methyl cyanide (20 ml.) A red solution was produced and on the addition of anhydrous ether to this solution red crystals were precipitated, m.p. 91-93°C. (Found: C, 16.27; H, 4.20; Br, 12.94; I, 43.20. $C_8H_{24}N_4AsBrI_2$ requires: C, 16.4; H, 4.1; Br, 13.65; I, 43.4).

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